

California Environmental Protection Agency

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Northern Laboratory Branch

Monitoring and Laboratory Division

**SOP No. MLD 032**

**STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF  
NON-METHANE ORGANIC COMPOUNDS IN AMBIENT AIR BY GAS  
CHROMATOGRAPHY USING DUAL CAPILLARY COLUMNS AND FLAME  
IONIZATION DETECTION**

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**State of California  
CALIFORNIA AIR RESOURCES BOARD  
MONITORING AND LABORATORY DIVISION  
SOP No. MLD 032  
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**STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF NON-METHANE  
ORGANIC COMPOUNDS IN AMBIENT AIR BY GAS CHROMATOGRAPHY USING DUAL  
CAPILLARY COLUMNS AND FLAME IONIZATION DETECTION**

**1. SCOPE**

This document describes the method for analysis of non-methane organic compounds (NMOG) in ambient air. The method is developed from and based upon EPA-600/625/R-96/010b and SOP No. MLD032 Revision 3.1. Method MLD032 is a modified version of USEPA Compendium Method Toxic Organics TO-14(A). It involves the cryogenic pre-concentration of volatile organic compounds (VOCs), of which many are involved in photochemical formation of ozone in atmosphere. VOCs are defined as aliphatic and aromatic compounds having a vapor pressure greater than 0.10 Torr at 25°C and 760 mm Hg. The Environmental Protection Agency (EPA), under Section 182 of the 1990 Clean Air Act Amendments (CAAA) revised the air quality surveillance regulations in Title 40 Part 58 of the Code of Federal Regulations (40 CFR Part 58) to include provisions for the States to establish Photochemical Assessment Monitoring Stations (PAMS) as part of a State Implementation Plan (SIP) in ozone non-attainment areas classified as serious, severe, or extreme. This method addresses 56 recommended target compounds (range of C<sub>2</sub> through C<sub>12</sub>, Table 1 pg. 23) to satisfy the requirements of 40 CFR Part 58, Subpart E. This method is applicable to most conditions encountered in the sampling of whole air samples into SUMMA<sup>TM</sup> passivated stainless steel canisters, and also addresses water removal by Nafion<sup>TM</sup> dryer before analysis.

**2. SUMMARY OF METHOD**

Ambient air is sampled over a three-hour period and collected in a clean SUMMA<sup>TM</sup> passivated stainless steel canister that has been evacuated. A pressurize mode, using a XonTech 910A sampler, is used during sample collection. A sample of air is drawn through a sampling train that regulates the rate and duration of sampling. A record of field information is sent back to the Northern Laboratory Branch (NLB) of the Organics Laboratory Section (OLS) along with the sample for immediate analysis. Upon arrival to the laboratory, the canister sample is equilibrated to room temperature for at least one

hour before the pressure is checked using a calibrated gauge. All information from the canister is documented in the login protocol, as well as into Laboratory Information Management Systems (LIMS).

A 300 cc ambient air sample is introduced into the automated Gas Chromatography (GC) system from the pressurized canister to the concentrator through 1/16" stainless steel tubing with the aid of a Mass Flow Controller (MFC) and a vacuum system. The MFC digital meter readout that is attached to the Sierra MFC within the GC provides a visual indication of the proper sample flow during sampling. Automated sampling of up to 16 canister samples can be accomplished using a multi-position automated sampler. The sample passes through the Nafion™ dryer to remove moisture (H<sub>2</sub>O vapor) from gas streams without the loss of PAMS target compounds. The dried sample is trapped within 1/8" nickel tubing filled with silanized glass beads (60/80 mesh) at -172°C. The desired NMOC components are immobilized (solidified), while oxygen (O<sub>2</sub>), carbon monoxide (CO), and methane (CH<sub>4</sub>) pass through the vent. The sample in the trap is purged with nitrogen (N<sub>2</sub>) followed by isolation, rapid heating and injection onto the column.

### **3. INTERFERENCES AND LIMITATIONS**

- 3.1** All compounds are identified by their corresponding retention times. Compounds in ambient air that have similar retention times may co-elute causing inaccurate quantifications, as well as misidentification.
- 3.2** Excess moisture, especially with large sample volumes, not removed by an in-line Nafion™ dryer and trapped with the sample can interfere with the Flame Ionization Detection (FID) signal, producing an elevated baseline and tailing. Correction by data system integration can offset most of these effects. Also, high levels of water can cause trap blockage, which prevents complete sample loading. Blockage can be detected by elevated pressure readings on purge gases during trap flushing. Injecting smaller sample volumes can minimize this problem.
- 3.3** Due to possible carryover effects, a blank analysis should be performed immediately after analyzing samples with high concentrations of VOCs (i.e., outside the calibration range).
- 3.4** Insufficient cooling within the cryotrap during the pre-injection period may cause inefficient trapping of organic compounds, especially C<sub>2</sub> compounds and propane. Check to ensure that during the thermal stabilization period that the trapping temperature reaches -172°C and is maintained. If the trap temperature deviates well below the set temperature, CH<sub>4</sub>, O<sub>2</sub>, and CO<sub>2</sub> can be trapped and cause detector

problems. CH<sub>4</sub> and O<sub>2</sub> can cause baseline perturbations, and CO<sub>2</sub> can cause plugging problems.

- 3.5** Improper use of the MFC, especially when introducing a specific sample volume into the system, will produce significant errors in the final results. Periodically observe the MFC's actual sampling rate from the MFC's digital flow meter readout to ensure that there is agreement, and that these settings are at the calibrated range for the instrument. It should also be noted that air streams with high levels of CO<sub>2</sub> (>10%) can cause significantly lower volumes to be sampled, and should not be used with MFC sampling.
- 3.6** Other typical problems encountered are dirty FID jets, plugged jets, and improper flame gas flows. Optimization, involving setting the carrier, hydrogen, and makeup gases, should be performed whenever the peak signature changes (peak broadening, multiple peaks, and significant changes in retention times). It is also important that the optimal instrument settings are recorded and maintained. In addition, preventive maintenance should be performed at least once a year.

#### **4. APPARATUS**

- 4.1** An Ultra-Trace Hydrocarbon System (UTHS), employing a Varian Model 3600Cx (GC) system (from Lotus Consulting) equipped with the following:
- i.** Automated sampling hardware (16-port multi-position automated sampler), consisting of an 8134 multi-position Stream Selector Valve (SSV).
  - ii.** Gas pneumatics with High Performance Valves (Valco Instruments-high temperature, low internal volume version with operating temperature, range of +100°C to 350°C).
  - iii.** Inert nickel contact surfaces and low-volume nickel or stainless steel interconnecting tubing. Examples of tubing size and material are 1/8 inch Teflon tubing, 1/16 inch stainless steel tubing, 1/16 inch nickel tubing, or 1/16 inch glass lined stainless steel tubing.
  - iv.** 1/8" nickel tubing concentrator trap (inner volume approx. 0.500 ml) with adsorbent silanized glass beads (60/80 mesh).
  - v.** Three capillary columns, a J&W Scientific 15m DB-1 and a 60m DB-1 with 0.32mm ID, 1 micron film thickness, and a Chrompack 50m Al<sub>2</sub>O<sub>3</sub>/Na<sub>2</sub>SO<sub>4</sub>

Porous Layer Open Tubular (PLOT) capillary column with 0.32mm ID, 5 micron film thickness.

- vi. Dual FIDs, both composed of 0.02" ceramic flame tips.
- vii. A continuous self-regenerating dryer (Nafion™, Perma Pure Inc.).
- viii. High performance digital flow controllers for accurate and reproducible flow regulation. A pressure regulator is set in parallel with the flow controller to minimize flow upsets during valve switching and to prevent system pressure from dropping below the set pressure. The digital flow controllers and pressure regulator are installed in the heated pneumatics compartment, which is heated isothermally to 45°C.

**Note:** *Pressure gauges or Electronic Pressure Readouts (EPRs), give a visual display of column pressure and are used for carrier gas monitoring and problem diagnostics (displayed on the pneumatics panel in front of the GC).*

- ix. A Sierra Model 840 MFC (0-5 VDC output) calibrated to deliver a constant flow rate from 0 to 100 sccm/min  $\pm$  3% for N<sub>2</sub> or air with an inlet pressure of 80 psig. The MFC readout display (Sierra Instruments, Inc.) is set at 50% of the 100-sccm/min output or 50 sccm/min for flow control. The MFC is mounted downstream of the 8134 SSV to eliminate any contamination and to reduce dead volume in lines from sample trap.
- x. An inline (GC grade i.e., with a Teflon-lined stainless steel diaphragm) sample pressure regulator ("Go" Valve), to minimize pressure upsets during sampling.

**4.2** Carrier Gas Filter Supelpure™ HC 2-2445 and Sulpelpure™ O<sub>2</sub> 2-2449 or equivalent.

**4.3** Varian Star Chromatography Workstation software, PC based, IBM compatible, for GC system control, automation, and method editing. For a detailed description of Star Chromatography Workstation, See Appendix III.

**4.4** A Perkin-Elmer Nelson (PE) Data Station, including an Intel based PC and PE-Nelson 2700 /Turbochrom™ Chromatography data system, for data collection, storage, and quantitation. For a detailed description of Turbochrom™ -PE Nelson 2700 Data System, see Appendix II.



- 4.5 A Perkin-Elmer Nelson 900 Series Analog/Digital Converter (Model 970) that converts the GC's analog detector signal to digital data and stores the digital raw data for the future transfer to the PE Data Station.
- 4.6 Leak-free stainless steel canisters of the desired volume (e.g., 6L), with interior surfaces treated by the SUMMA passivation process.
- 4.7 A vacuum pump that can continuously draw air through the inlet manifold at a rate greater than 10L/min.

## 5 MATERIALS

- 5.1 A system blank, consisting of either zero air, Grade 5 ultrapure N<sub>2</sub>, or headspace (vent) liquid N<sub>2</sub>.
- 5.2 A Standard Reference Material 1800 (SRM-1800), certified by the National Institute of Standards and Technology (NIST), containing fifteen Toxic VOCs in N<sub>2</sub> (Table 2, pg. 24), is used for daily one-point calibrations of the GC instruments. All concentrations are given in a molar ratio for a given compound, relative to the total of all constituents or nanomole/mole (parts per billion - ppb). Trace hydrocarbon concentrations have been assigned units of **ppb Carbon (ppb C)**. This unit is derived by multiplying ppb volume/volume (ppb v/v) by the number of carbons in the molecule of analyte. In our dual column GC system, the C<sub>2</sub>-C<sub>4</sub> compounds are calibrated with **Propane (C<sub>3</sub>)** and C<sub>5</sub>-C<sub>10</sub> are calibrated with **Benzene (C<sub>6</sub>)**. This NIST mix is also used in multipoint analysis to establish a linear dynamic range, as well as the Limit Of Detection (LOD) of the instrument.
- 5.3 A control sample, PAMS Retention Time cylinder (e.g., CC60089 - Spectra Gas Supply Inc., Alpha, NJ), containing 56 components, is used for retention time calibration and daily quality control.
- 5.4 Nitrogen, Grade 5 or ultra-pure is used as a FID make-up gas, fore-flushing gas, and as a counter-flow drying gas in the Nafion™ dryer.
- 5.5 Helium, Grade 5 or ultra-pure is used as a carrier gas.
- 5.6 Helium, Grade 5 or lower purity, is used as a valve actuator gas.
- 5.7 Liquid Nitrogen (LN<sub>2</sub>) is used for cryogenic preconcentration and sub-ambient GC analysis. Also, headspace LN<sub>2</sub> (vent) is used for system blank analysis.
- 5.8 Hydrogen, Grade 5 or ultra-pure is used as a detector fuel gas.

- 5.9** Zero Air, is used as a flame ionization detector oxidant.
- 5.10** High Performance Liquid Chromatography (HPLC) grade water (150 $\mu$ L H<sub>2</sub>O in 6L canister) is used for humidification of the standard hydrocarbon mix, the control mix, and any other in-house hydrocarbon gaseous mixtures injected into SUMMA™ passivated canisters. This is done in order to simulate humidified ambient air samples, as well as minimize active surface sites inside the canister.
- 5.11** Isopropyl alcohol/water (1:1) is used for leak detection (external applications only).

## **6 INSTRUMENT CONFIGURATION AND PARAMETERS**

- 6.1** The analytical system and automation configurations are shown in Figures 1, 2, and 3. The valving diagrams depict the system configuration for normal operation including the use of a MFC for sample introduction and the use of 8134 SSV relay for ports 1-16 of the autosampler. Valves A, B, C and D are configured to *off* positions (-) for normal operation i.e., ready/standby. On the left side of the GC instrument there is a switch for manual sample purge, which activates relay +3 and turns valve B *on*. This can be used to manually condition the sample lines, evaluate MFC output flow, or to set the pressure of the inline “Go” valve. Also located on the left side panel of the GC instrument is a toggle switch that operates valve B. This toggle switch is normally set to the “disable” position since all calibrations are done by external standard analysis, but it can be set to “enable” for an internal standard/spike sample analysis. On the right side of the GC instrument there is a button for manually advancing the stream selector valve for ports 1-16. This option is used when leak-checking and/or troubleshooting the alignment of streams in the 16-port valve.
- 6.2** There are six separate temperature zones for which there are parameters entered in Star Workstation: **GC Injector A** (not used), **GC Injector B** (Cryotrap), **GC Auxiliary** (Valve B, C, D), **GC Column** (Valve A, Analytical Capillary Columns), **GC Detector Heater A** (FID), and **GC Detector Heater B** (not used). There is one additional external temperature zone for the 16-port 8134 SSV, set manually at 130°C.

**Note:** *The temperature setting for injector B does not correspond to the true temperature of the injector. A graph is provided (Figure 4) which illustrates the relationship between the injection setting in the Star Workstation, and the true temperature of the concentration trap.*

### **6.3 Sample Volume Injection**

A sample volume of 300 standard cubic centimeters (sccm) is achieved by collecting the sample for 6.00 minutes at a rate of 50 sccm/min. The process for achieving the proper volume of sample for injection is fully automated by the use of a Relay Time Program, which is part of the Varian GC Star Chromatography Workstation software, version 4.51. The location of the valves for a Varian 3600 Cx GC analytical system as well as the layout for the pneumatic controls is shown in Figure 1. Table 3A lists the relays and their corresponding functions. Table 3B lists the valve actuators employed in this system along with their corresponding degree of rotation.

#### 6.4 3600GC Running Parameters:

- 6.4.1 GC Injector A** is not used. Injectors A and B must be specified as **on** and set to **temperature programmable** to ensure proper hardware description. GC Injector B is the cryotrap. The cryotrap has a volume of approximately 500  $\mu\text{L}$ . This low volume facilitates a rapid heating/cooling cycle (from  $-172^{\circ}\text{C}$  to  $200^{\circ}\text{C}$ ) with minimum temperature overshoots/undershoots at set points. A typical temperature profile of a concentrator trap is shown in Figure 5.
- 6.4.2 GC Auxiliary** oven is used to maintain the three Gas Sampling Valves (GSV) B, C and D at a constant temperature. GC Auxiliary oven must be set with a high enough temperature to ensure that there is no sample condensation (max. temp.  $\leq 350^{\circ}\text{C}$ ).
- 6.4.3 GC Column Oven** contains GSV A and all the analytical capillary columns (three capillary columns, a J&W Scientific 15m DB-1 pre-column, and a 60m DB-1 with 0.32mm ID, 1 micron film thickness and a Chrompack 50m  $\text{Al}_2\text{O}_3/\text{Na}_2\text{SO}_4$  PLOT capillary column with 0.32mm ID, 5 micron film thickness analytical columns). The GC Column A Parameters and the GC Column B Parameters in the method **do not** alter or control any setpoints in the GC. GC Column parameters are given in the Star Chromatography Workstation GC 3600 Module of the analytical method in order for the instrument to calculate the linear velocity of the carrier gas and other base-level parameters (the pressure readings from the digital electronic pressure readouts) prior to analysis.
- 6.4.4** There are two FID **GC Detectors**, one for each analytical column. Only one heating block is used in our GC (Heater A), which contains both Detector A and Detector B. There is no Heater B. However, settings for both Heater A and Heater B are entered in Star Chromatography Workstation because this is necessary in order for the software to run properly. Also, settings are entered for the **attenuation** that is only used for stripchart recorders. Attenuation parameters in the method have no effect on the signal output to either the Star or PE-Nelson Chromatography Data Acquisition systems.
- 6.4.5 GC Autosampler** designates the 8134 multi-position Stream Selector Valve as the input source for samples into the system.

**6.4.6 GC Relays Time Program** is the post injection relay time program. This portion of the method contains the time setpoints for activating relays, which in turn control the various valves used in the GC:

Relay Time Program? : Use

	<u>Time(min)</u>	<u>Relay#</u>
Start Oven temp. program	0.00	- - - -
Isolation of the trap/heat trap	0.01	- - - +4
Injecting sample onto PLOT	1.50	- - - -
Injecting sample onto DB-1	3.40	+1 - - -

**[X]** Return Relays to Initial Conditions at Run End

**6.4.7** There is no **stripchart recorder** attached to the instrument. Printed output is obtained through the Star GC Workstation and Star Chromatography software.

**6.4.8** The current gas flows and regulator pressures are shown in **Appendix I**. The Gas Flow Settings and output Gas Cylinder Pressures are only to be used as guidelines and not as absolute values. Optimal flows should be determined individually for each GC analytical instrument.

## 7. NMOC SPECIATED ANALYSIS PROCEDURE

### 7.1 Sample Pre-Injection Period (PIP)- Figures 2A through 2F

Ambient air, calibration standards and control samples in SUMMA™ passivated canisters are connected to the autosampler using appropriate tubing and fittings. To evacuate or purge the lines manually, press the manual sample purge button located on the left side of the instrument panel (which rotates valve B to the *on (+3)* position). After assuring the connections are leak-free, the valves of the sample containers can be opened.

**7.1.1** The GC 3600Cx system configuration and GC operational editing functions (sample list file-**.smp**, sequence file-**.seq**, and method file-**.mth**) are done in the Star Chromatography 3600 Workstation (Version 4.51). See Appendix III.

**7.1.2** PE-Nelson 2700 data system (Turbochrom Ver. 4.1.2f12) is set up for data acquisition, storage, and integration. See Appendix II.

- 7.1.3** The sampling flow rate is set and measured using a MFC (Sierra Instruments, Inc.), which is mounted downstream of the sampling point to eliminate any contamination and to reduce dead volume in lines from sample trap. The sample amount in terms of volume (standard cubic centimeter-sccm) is:

$$\text{Volume} = [\text{Trapping Time}] \times [\text{Flow Rate}]$$

I.e., Volume = [6.00 min] x [50.0 sccm/min] = 300 sccm

- 7.1.4** The PIP system configuration for normal operation (all valves in *off* position ) is set for external standard calibration and for MFC sampling (Figure 2A). Standard, control, and ambient air samples are introduced into the GC from an automated relay time program set in the Star Chromatography Workstation. The PIP time, relay, and events are edited in the sample list file (**.smp**) and are set as follows:

Time	Actuation Events	Valve Events
------	------------------	--------------

<b>0.00 min</b>	- - - -	All events are set to the <i>off</i> (-) position. This is the standby/ready position. The sample (Sx) passes through the inline "Go" valve Sx pressure regulator, set at approximately 5.0 psig, through the Nafion™ dryer, and then dead-ends at port 7 of valve B. The N <sub>2</sub> purge gas flows through the sample loop of valve B, through valve C, through valve flowmeter and into the vacuum. Primary He gas is directed through valves C and D, through the cold trap, through valve A, through the capillary precolumn, through the PLOT column, and into the FID detector A. Secondary He is directed through DB-1 column onto the FID detector B. See Figure 2A.
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Time	Actuation Events	Valve Events
------	------------------	--------------

<b>0.01 min</b>	- - +3 -	Valve B, is <i>on</i> (+3), allowing sample flow through the MFC and out to vacuum. This conditions the lines by purging them with the new sample, and also allows time for the MFC to stabilize at 50 sccm/min. See Figure 2B.
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<b>1.00 min</b>	- +2 +3 -	Valve B and C are activated to the <i>on</i> position (+3, +2). The sample flow is directed through injector B (cryotrap), which is at -172 <sup>0</sup> C. At this point effective sample loading begins. See Figure 2C.
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<b>7.00 min</b>	- +2 - -	Valve C is <i>on</i> (+2) and valve B is <i>off</i> (- 3). Effective sample loading is terminated. The sample flow dead-ends, allowing N <sub>2</sub> to purge the sample in the trap and the interconnecting lines of any gases that are bound to surfaces (e.g., O <sub>2</sub> , CO, CH <sub>4</sub> ). These gases will be flushed by N <sub>2</sub> through the MFC and then out to the vacuum.
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**Note:** By controlling the timed events activating valve B (+3) and turning off valve B (-3), the sample volume can be varied. See Figure 2D.

<b>7.30 min</b>	<b>- +2 - +4</b>
-----------------	------------------

Valve B is deactivated (-3) and valve C and D are *on* (+2, +4). The trap (injector B) is isolated and N<sub>2</sub> is redirected through the MFC, through the flow meter, and out to vacuum. Activation of valve D (+4) prompts PE Nelson 2700 to begin acquiring data (Turbochrom Chromatography Workstation, ver. 4.1.2f12). See Figure 2E.

<b>7.35 min</b>	<b>- - - +4</b>
-----------------	-----------------

Valve C is deactivated (-2) and valve D is *on* (+4). The trap (injector B) remains isolated and the GC system is ready for the positive time events or post-injection period. See Figure 2F.

## 7.2 Sample injection/post-injection period (Figures 3A-3C)

**7.2.1** All timed events for post sample injections are edited in \*.**meth** files with Method Editor in the Star Chromatography 3600 Workstation.

Time	Actuation Events	Valve Events
------	------------------	--------------

<b>0.01 min</b>	<b>- - - +4</b>
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Valve D is *on* (+4). The trap is isolated while being heated to 200<sup>0</sup>C (set at 250 at the rate of 250<sup>0</sup>C /min). See Figure 3A.

<b>1.50 min</b>	<b>- - - -</b>
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Valve D is *off* (-4). The trap is open and in series with the PLOT column i.e., the heated sample is purged by primary He into the GC oven, through the DB-1 pre-column where the C<sub>2</sub>-C<sub>4</sub> compounds are separated from the C<sub>5</sub>-C<sub>12</sub> compounds and are injected onto the PLOT column. See Figure 3B.

<b>3.40min</b>	<b>+1 - - -</b>
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The trap is in series with the DB-1 column *via* actuation of valve A (+1), the C<sub>5</sub>-C<sub>12</sub> compounds are carried through the DB-1 pre-column and injected directly onto the DB-1 analytical column. This timing may require adjustments due to changes in columns and/or column flows. The switch is made to allow 1,3-butadiene to be last component eluting off of the Alumina PLOT column. See Figure 3C.

## 8. DATA ANALYSIS

In general, the sequence of analysis for Engineering Laboratory Branch methodology, including the requirements of quality control, is as follows:

1. System blank
2. Calibration
3. Control sample
4. Ambient samples
5. Sequence duplicate/replicate
6. Check or cross-duplicate sample

- 8.1** A system blank, consisting of either ultrapure zero air, headspace liquid nitrogen, or ultrapure N<sub>2</sub> gas, is analyzed prior to calibration to detect system contamination. System blanks must not have any interfering peaks greater than the LOD (1.0 ppb C) for any individual analyte of interest before proceeding to the next step.
- 8.2** A daily system calibration is performed with a 15 component certified NIST33762, SRM 1800-14A externally traceable primary gas standard mix (Figure 6A page 37 and Figure 6B page 38). The standard is prepared in a humidified (injection of 150 microliters of HPLC grade water under vacuum) SUMMA™ passivated canister that is analyzed after a system blank and before any ambient samples. The NIST standard offers certified concentrations for **propane** and **benzene** in concentrations applicable to ambient air analysis. A single point calibration is established for each sequence using a single analysis of the external standard at 300-sccm (mL) volume. There is no “averaging” of the daily response factors. The FID detector response, in area counts, is directly related to a known concentration of the analyte (i.e., propane and/or benzene), and is used to calibrate the instrument each time it is used. After the analysis of the standard run, the response factor (Rf) is calculated as follows:

$$\begin{aligned} \text{Rf} &= (\text{Std. Conc.}) / \text{Std. Area Count} \\ \text{i.e., Propane} &= (16.2 \pm 0.6 \text{ ppb C}) / \text{Area Count} \\ \text{i.e., Benzene} &= (31.2 \pm 1.2 \text{ ppb C}) / \text{Area Count} \end{aligned}$$

**Note:** The concentrations of propane and benzene in the NIST SRM 1800 standard mix are listed as  $\pm 0.2$  nmole/mole. This uncertainty is due to imprecision in the preparation and analysis of the standard.

- 8.3** A control sample (1997 PAMS Retention Time cylinder, Spectra Gas Supplies Inc.) is analyzed before any ambient air samples and is used for retention time calibration and for daily quality control (Figures 7A, 7B). This gas mixture contains 56 compounds (C<sub>2</sub>-C<sub>12</sub>), of which 14 compounds are evaluated as daily control limits, as defined in the MLD

Laboratory Quality Control Manual, Revision 2.3 (1997). Each control sample result is plotted daily on a control chart (Table 7).

- 8.4 Ambient samples are introduced and analyzed under the same conditions as the calibration standard and the retention time standard. The resultant peaks are identified by their retention times and quantified using the Rfs calculated with the certified values of propane (PLOT) and benzene (DB-1) in the NIST standard.
- 8.5 Duplicate analyses (analysis of the same sample by the same instrument) are performed on at least 10% of the ambient samples analyzed. Data for concentrations in excess of the limit of detection ( $\geq$  LOD) are recorded. The percent difference of the duplicate analyses are recorded, and values that are  $\geq 5X$  LOD and exceed the maximum percent difference (see 9.03 for formula) for an analyte are included in the Quality Control report.
- 8.6 Cross duplicate analyses (analysis of the same sample by different GC instruments) are performed on at least 10% of all ambient samples. Cross duplicate analyses are evaluated under the same conditions as the duplicate analyses.

## 9. QUALITY CONTROL

- 9.1 A system blank consisting of either humidified Ultra-pure zero-air, or Grade 5 N<sub>2</sub> is run once daily prior to calibration to check for any system contamination (background). A system blank must also be run after any sample that contains high concentrations of analytes (exceeding the linear range of the detection), to eliminate any possible carry-over and bias on the next analysis in the sequence. If the system blank contains any interfering peak that is greater than 1.00 ppb C for any targeted analyte, or the sum of all targeted peaks for both analytical columns exceeds 20 ppb C (or 10 ppb C per column ) the following corrective actions will be taken:
  - 1. Check system for leaks: Most contamination that is observed in the system blank is due to leaks, especially when the gases that serve the GC instrument have been changed. Look for obvious sources of contamination, especially the items that have been changed recently.
  - 2. Clean system with wet air: Purging out the GC system with several runs of humidified air to reduce and to eliminate any source of contamination in order to meet the acceptable criteria for system blank.
  - 3. Bake-out sample trap/system: Run the GC system with the zones at elevated temperatures.
  - 4. Repeat analysis.



**9.2** Prior to the analysis of ambient samples, but after the system blank, single point calibration (daily calibration) is performed. The NIST standard (SRM 1800-14A) provides propane and benzene as certified externally traceable primary standards for calibrating the PLOT and DB-1 columns respectively. The acceptance criterion for daily calibration is that the calculated Rf value must be within  $\pm 10$  relative percent difference (RPD) of the average Rf for each calibrating compound. Attention must be given to changes in Rf values that may indicate instrument, standard gas mix, or detector sensitivity changes. The following corrective action should be made if the above criterion is not met:

1. Repeat daily calibration analysis.
2. Check FIDs for leaks and check gas flows: Detector sensitivity changes are mostly attributed to leaks in the detector and changes in gas flows. Make sure that the gas cylinder pressure requirements are met and that the gas flow settings have not been altered. If all the settings are correct, but the flow requirements are not met, check for the leak source and correct the problem. Document the corrective action taken, and repeat the daily calibration analysis.
3. Prepare new calibration standard sample and repeat the analysis: Prepare a new NIST standard sample (humidified with 150 $\mu$ L H<sub>2</sub>O) and re-run the daily calibration.
4. Repeat multi-point analysis: If all the corrective actions listed above do not produce the desired result, then verify the linear dynamic range of the FID detectors by preparing and running new calibration standards. Verify that the expected precision, accuracy, and LODs are also not compromised. The calculated precision, accuracy and the LODs must be equal to or better than the established criteria prior to the PAMS season.

**9.3** A control sample (1997 PAMS Retention Time cylinder, Spectra Gas Supplies Inc.) is analyzed before any ambient air samples and is used for retention time calibration and for daily quality control. This gas mixture contains 56 compounds (C<sub>2</sub>-C<sub>12</sub>), of which 14 compounds are evaluated as daily control limits and are plotted daily on a control chart. Control limit levels are established based on calculated standard deviation (std) of at least 20 measurements of the control sample analyzed during the pre-season period. The limits are set as follows:

UCL (Upper Control Limit)	=	+3*std of Mean Value
UWL (Upper Warning Limit)	=	+2*std of Mean Value
Mean	=	Assayed Value
LWL (Lower Warning Limit)	=	-2*std of Mean Value

$$\text{LCL (Lower Control Limit)} = -3 \times \text{std of Mean Value}$$

If results of the control sample fall outside the Control Limits (UCL/LCL) for any compound, the control sample is reanalyzed. If the second results are also outside of the Control Limits, the analysis is discontinued, the Supervisor notified, the cause of the problem is investigated, and all data collected for that sequence is invalidated for those particular compounds that are outside the Control Limits.

An additional QC check of retention time windows for all 14-target analytes is performed using a retention time standard (control sample). This provides a comprehensive check of retention time windows and peak identification for all target VOCs.

- 9.4** Duplicate analysis of ambient samples is performed daily on at least 10% of the total ambient samples analyzed. The Relative Percent Differences (RPD) of duplicate results for each target compound are recorded. The Maximum Allowable Percent Difference (MAPD) for any analyte with a concentration equal to or greater than 5.0 ppb C is 25%. If any targeted compounds fail to meet this criterion, the results of the compound are invalidated for the whole sequence.
- 9.5** Cross duplicate analyses (using the same method of analysis of the same sample by different GC instruments) are performed on at least 10% of the total samples analyzed. The cross duplicate table is updated weekly (all target compounds  $\geq$  LOD are recorded). The same acceptance criterion used for duplicate analyses is applied for cross duplicate analysis.

## **10. METHOD SENSITIVITY, PRECISION, AND ACCURACY**

- 10.1** Multipoint analysis must be performed prior to the start of the NMOC season to verify the linear dynamic range of the FID response (Table 5A-Propane, Table 6A-Benzene). Hydrocarbon concentrations in ambient air can vary over a wide range, from very low ppb C to ppm C (parts per million). A strong positive correlation over the expected operating range ensures accurate results. FIDs usually exhibit linearity over a  $10^7$  range (range set is  $10^{-12}$  amps/millivolts at 50-microsecond time constant for speciated NMOC analysis). Multipoint analysis is performed with at least four (4) concentration levels over the linear range of the instrument. Each concentration level is measured at least three (3) times. A linear regression analysis is performed using concentration and average area counts to determine the regression correlation coefficient ( $r$ ). The linearity of the calibration curve is verified when the coefficient  $r$  is greater than 0.98. If an ambient concentration of any compound exceeds the defined linear range of that compound, the sample must be diluted (so that the diluted component has a detector

response within the defined linear range), reanalyzed, and the concentration recalculated for that particular compound.

- 10.2** As defined in the Laboratory Quality Control Manual, Revision 2.3 (1997) the Limit of Detection (LOD) is the Method Detection Limit (MDL), which is the minimum concentration of a substance that can be measured and reported with 99% confidence. The MDL is given in the *Code of Federal Regulations* (40 CFR 136 Appendix B) as the product of the standard deviation (seven replicate measurements of the analyte of interest at a concentration near but less than 5 ppb C) times the expected detection limit (1 ppb C) and the value of 3.14 ( $t_{(n-1, \text{conf.} = 99\%)}$  student t value for 99% confidence for seven values). See Table 4.

$$\text{LOD} = t_{(n-1, \text{conf.} = 99\%)} \times S$$

$t_{(n-1, \text{conf.} = 99\%)}$  = student's T-distribution value at n-1 degrees of freedom

S = standard deviation

$$\text{LOD} = 3.14 \times [S_7]$$

The published LODs for this method are:

All Target VOCs..... <1.0 ppb C

Multipoint calibration and LOD calculation must be performed under each of the following conditions:

- a.) prior to every NMOC season
  - b.) when system maintenance is performed
  - c.) when minor modifications are done that may change the expected precision accuracy, and/or LOD of the measurement
  - d.) when a major modification is performed that may change the analytical equipment configuration, operating conditions, analyte target list, change in matrix or reagents that may change the precision, accuracy, and LOD calculation.
- 10.3** A duplicate/replicate analysis is the analysis of the same sample twice in one sequence. Duplicate samples are chosen at random, and should account for at least 10% of the total ambient samples analyzed. Method variability can be estimated from duplicate measurements. To make a comparison of two values, Percent Difference (%D) is a more meaningful statistic than RSD. The duplicate/replicate pairs are evaluated based on the following formula:

$$\%D = \frac{|y - x|}{(y + x)} \times 200$$

Where %D is the percent difference, the x and y represents the corresponding concentrations of an analyte for original and duplicate analyses.

- 10.4** The QA section provides the laboratory with performance audits (reference standards submitted in canisters as “blind” audits) to assess the accuracy of the data generated by the instrumentation. A measure of analytical accuracy is the degree of agreement with audit standards. Audit accuracy is defined as the difference between the nominal concentration of the audit compound and the measure value divided by the audit value, and is expressed as a percentage, as illustrated below:

$$\text{\%Audit Accuracy} = [(\text{Audit Value} - \text{Measured Value}) / \text{Audit Value}] * 100$$

The reference value for an accuracy standard should be a certified reference material (CRM) or traceable to a standard reference material such as a NIST Standard Reference Material (SRM). Federal regulations require State and Local air monitoring agencies to perform annual accuracy checks.

## **11.0 METHOD REVISION HISTORY**

### **11.1 SOP No. MLD 032 Revision 1.0/1.1 (1989-1992):**

- a. Method developed from and based on EPA/600-8-9/215 Document.
- b. Instruments: Perkin-Elmer (PE) 8500 GC system with an EnTech Concentrator; Hewlett-Packard (HP) 5890 GC system with NuTech 3550; PE Nelson 2600 data system (IBM based).
- c. Reagents: NIST propane standard (CC8374) with 2.0 cm<sup>3</sup> of 295.2 ± 3.0 pphm C for daily system calibration (MLD 032 revision 1.0); seven - component NIST Standard Mix including propane and hexane for daily system calibration (CC24324, MLD 032 revision 1.1); a 35-component (CC68695) Retention Time Standard; Dual-column analytical system (introducing PLOT column) with two FID detectors (MLD 032 revision 1.1).

### **11.2 SOP No. MLD 032 Revision 2.0 (1992-1994):**

- a. Method developed from and based on EPA/600-8-9/215 Document and SOP No. MLD 032, revision 1.1.
- b. Instruments: Perkin-Elmer (PE) 8500 GC system with NuTech 3550 cryogenic air pre-concentrator unit equipped with a sixteen-port autosampling valve; Dual column configuration (J&W 60m x 0.32mm DB-1 and Chrompack 50m x 0.32 Al<sub>2</sub>O<sub>3</sub>/Na<sub>2</sub>SO<sub>4</sub> PLOT) with two FIDs; PE Nelson 2600 data system (IBM based).

c. Reagents: NBS SRM 1665b, propane in air at 2.87 ppmv, used as the calibration check; seven- component NIST Standard Mix including propane and hexane for daily system calibration (CC24324); a 35-component (CC68695) Retention Time Standard.

d. Temperature zones are defined:      Transfer lines:      75<sup>0</sup>C  
Valve Oven:      50<sup>0</sup>C  
Cryotrap:      -170<sup>0</sup>C to 150<sup>0</sup>C

e. Temperature Ramping for GC oven is defined:

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
Oven T ( <sup>0</sup> C)	-10	8	138	200
IsoTime- min	5.5	0.0	0.0	5.0
Ramp rate ( <sup>0</sup> C/min)	1.0	2.5	30.0	

### **11.3 SOP No. MLD 032 Revision 3.0/3.1 (1996-2001):**

a. Method developed from and based on EPA/600/625/R-96/010b Document.

b. Instruments: Varian UTHS Model 3600 Cx GC system equipped with 8134 multi-position Stream Selector Valve; Three column configuration (J&W 60m x 0.32mm DB-1, Chrompack 50m x 0.32 Al<sub>2</sub>O<sub>3</sub>/Na<sub>2</sub>SO<sub>4</sub> PLOT and J&W 15m x 0.32mm DB-1 pre-column) with two FIDs; PE Nelson 2600 (revision 3.0) and PE Nelson 2700 (revision 3.1) data system.

c. Reagents: NIST9023 (ALM009023) Calibration, 7-Component Standard Mix, with Propane (26.1 ppb C) and Hexane (28.2 ppb C) used as primary calibrating components for C2-C4 PLOT column and C5-C10 DB-1 column respectively (1996-1997, SOP No. MLD 032 revision 3.0); NIST33762 or NIST33759 (sister cylinders), a 14-Component SRM 1800 Standard Mix with Propane (16.2 ppb C) and Benzene (31.2 ppb C) used as primary calibrating components for C2-C4 PLOT column and C5-C10 DB-1 column respectively (1998-2001, SOP No. MLD 032 revision 3.1); PAMS Retention Time cylinder, ranging from 54 to 56 components.

e. GC Auxiliary heating zone changed from 125<sup>0</sup>C (ver. 3.0) to 175<sup>0</sup>C (ver. 3.1) to further eliminate any possible cold-spots or carry-over.

f. Activation of valve D (+4) in the sample pre-injection period (PIP) of 7.30 minutes, prompts the PE Nelson 2700 to begin acquiring data by Turbochrom Chromatography Workstation.

g. All FID detectors are equipped with 0.02" flame tips.

h. All other specifications and parameters are identical to both revisions.

**Table 1. PAMS Target VOCs**

USEPA National Exposure Research Laboratory  
Doc.: EPA/600-R-98/161

<b>AIRS Code</b>	<b>Target Name</b>	<b>AIRS Code</b>	<b>Target Name</b>
43203	Ethylene (Ethene)	43249	3-Methylhexane
43206	Acetylene (Ethyne)	43250	2,2,4-Trimethylpentane
43202	Ethane	43232	n-Heptane
43205	Propylene (Propene)	43261	Methylcyclohexane
43204	Propane	43252	2,3,4-Trimethylpentane
43214	Isobutane	45202	Toluene
43280	1-Butene	43960	2-Methylheptane
43212	N-Butane	43253	3-Methylheptane
43216	Trans-2-Butene	43233	n-Octane
43217	Cis-2-Butene	45203	Ethylbenzene
43221	Isopentane (2-Mebutane)	45109	m/p-Xylene
43224	1-Pentene	45220	Styrene
43220	N-Pentane	45204	o-Xylene
43243	Isoprene	43235	n-Nonane
43226	trans-2-Pentene	45210	Isopropylbenzene
43227	cis-2-Pentene	45209	n-Propylbenzene
43244	2,2-Dimethylbutane	45212	m-Ethyltoluene (1-Ethyl-3-Methylbenzene)
43242	Cyclopentane	45213	p-Ethyltoluene (1-Ethyl-4-Methylbenzene)
43284	2,3-Dimethylbutane	45207	1,3,5-Trimethylbenzene
43285	2-Methylpentane	45211	o-Ethyltoluene (1-Ethyl-2-Methylbenzene)
43230	3-Methylpentane	45208	1,2,4-Trimethylbenzene
43245	1-Hexene*	45238	n-Decane
43231	n-Hexane	45225	1,2,3-Trimethylbenzene
43262	Methylcyclopentane	45218	m-Diethylbenzene
43247	2,4-Dimethylpentane	45219	p-Diethylbenzene
45201	Benzene	43954	n-Undecane
43248	Cyclohexane	43141	n-Dodecane*
43263	2-Methylhexane	43102	TNMOC
43291	2,3-Dimethylpentane	43000	PAMHC

**Table 2. NIST Certified Concentration for SRM 1800-14-A**

Cylinder Number: ALM033762  
Certificate of Analysis: April of 1997

No.	Compound	nmole/mole	Uncertainty	Concentration (ppb C)
1	Ethane	5.0	$\pm 0.2$	10.2
2	Propane	5.0	$\pm 0.2$	16.2
3	Propene	5.0	$\pm 0.2$	15.6
4	Isobutane	6.0	$\pm 0.2$	22.0
5	n-Butane	5.0	$\pm 0.2$	21.2
6	Isobutene	6.0	$\pm 0.2$	22.0
7	2MeButane	6.0	$\pm 0.2$	29.0
8	n-Pentane	5.0	$\pm 0.2$	25.5
9	1-Pentene	5.0	$\pm 0.2$	25.5
10	n-Hexane	5.0	$\pm 0.2$	31.8
11	Benzene	5.0	$\pm 0.2$	31.2
12	n-Octane	5.0	$\pm 0.2$	40.8
13	Toluene	5.0	$\pm 0.2$	36.4
14	Ortho-Xylene	5.0	$\pm 0.2$	40.8
15	n-Decane	5.0	$\pm 0.2$	51.0

**Table 3A. Function of Valves for Varian GC 3600Cx System**

Non-Methane Hydrocarbon Analyzer – Operator's Manual

Lotus Consulting, Lotus Flower, Inc. 1995

<u>Valve #</u>	<u>Function</u>	<u>Event</u>	<u>Rotation</u>
<b>A</b>	Trap in series with PLOT	<b>-1</b>	Counterclockwise
	Trap in series with DB-1	<b>+1</b>	Clockwise
<b>B</b>	N <sub>2</sub> purge on	<b>-3</b>	Counterclockwise
	Sx flow on	<b>+3</b>	Clockwise
<b>C</b>	He carrier gas to trap	<b>-2</b>	Counterclockwise
	Sx to trap	<b>+2</b>	Clockwise
<b>D</b>	Trap in series	<b>-4</b>	Counterclockwise
	Trap is isolated	<b>+4</b>	Clockwise

**Table 3B. List of Valve Actuators for Varian GC 3600CX System**

Non-Methane Hydrocarbon Analyzer – Operator's Manual

Lotus Consulting, Lotus Flower, Inc. 1995

<u>Relay #</u>	<u>Number of Valve Ports</u>	<u>Actuator Rotation</u>
<b>A</b>	4	90 <sup>0</sup>
<b>B</b>	10	36 <sup>0</sup>
<b>C</b>	6	60 <sup>0</sup>
<b>D</b>	4	90 <sup>0</sup>



**Table 4. Calculated LODs and the Linear Range**

Method SOP MLD032

NIST Cylinder Number: ALM033762

Date of Analysis April 27, 1997				
<u>Compound Name</u>	<u>Upper Linear Range(ppbC)</u>	<u>Correlation Coefficient (r)</u>	<u>Calculated LOD (ppbC)</u>	<u>Published LOD (ppbC)</u>
Ethane	81.6	1.00000	0.06	<1.0
Propane	129.6	0.99999	0.07	<1.0
Propene	124.8	0.99998	0.22	<1.0
iso-Butane	176.0	0.99997	0.11	<1.0
n-Butane	169.6	0.99998	0.11	<1.0
iso-Butene	176.0	0.99998	0.12	<1.0
2-MeButane	87.0	0.99984	0.96	<1.0
1-Pentene	204.0	1.00000	0.16	<1.0
n-Pentane	204.0	0.99999	0.56	<1.0
n-Hexane	254.4	0.99998	0.76	<1.0
Benzene	249.6	0.99998	0.99	<1.0
Toluene	109.2	0.99911	0.77	<1.0
n-Octane	81.6	0.99990	0.70	<1.0
o-Xylene	81.6	0.99987	0.75	<1.0
n-Decane	153.0	0.99914	0.54	<1.0

**Table 5A. Multipoint Calculations for Propane**  
 Certified at 16.20<sub>ppb C</sub> - April 27, 1998

**NIST Cylinder Number ALM033762 – SRM 1800-14-A**

Vol. ccm [ X ] <sub>ppb C</sub>	25 1.35	75 4.05	100 5.40	200 10.80	300 16.20	450 24.30	600 32.40	900 48.60	1500 81.00	2400 129.60
<u>Area Counts-FID</u>	<u>Area</u>	<u>Area</u>	<u>Area</u>	<u>Area</u>	<u>Area</u>	<u>Area</u>	<u>Area</u>	<u>Area</u>	<u>Area</u>	<u>Area</u>
1 <sup>st</sup> Run	2800	8186	10974	22072	32886	49664	66741	100908	171683	268150
2 <sup>nd</sup>	2773	8212	11056	22229	32994	49693	67072	101323	171065	266835
3 <sup>rd</sup>	2758	8236	11041	22118	33416	49734	67000	101129	171398	265346
4 <sup>th</sup>	2786	8306	11029	22100	33106	49854	66846	101450	172185	
5 <sup>th</sup>	2840				33145					
6 <sup>th</sup>	2877									
7 <sup>th</sup>	2770									
[Mean] <sub>ppb C</sub>	2801	8235	11025	22130	33109	49736	66915	101203	171583	266777
[Std] <sub>ppb C</sub>	43	52	36	69	199	84	149	237	474	1403
%RSD	1.5	0.6	0.3	0.3	0.6	0.2	0.2	0.2	0.3	0.5
# of Observations	7	4	4	4	5	4	4	4	4	3

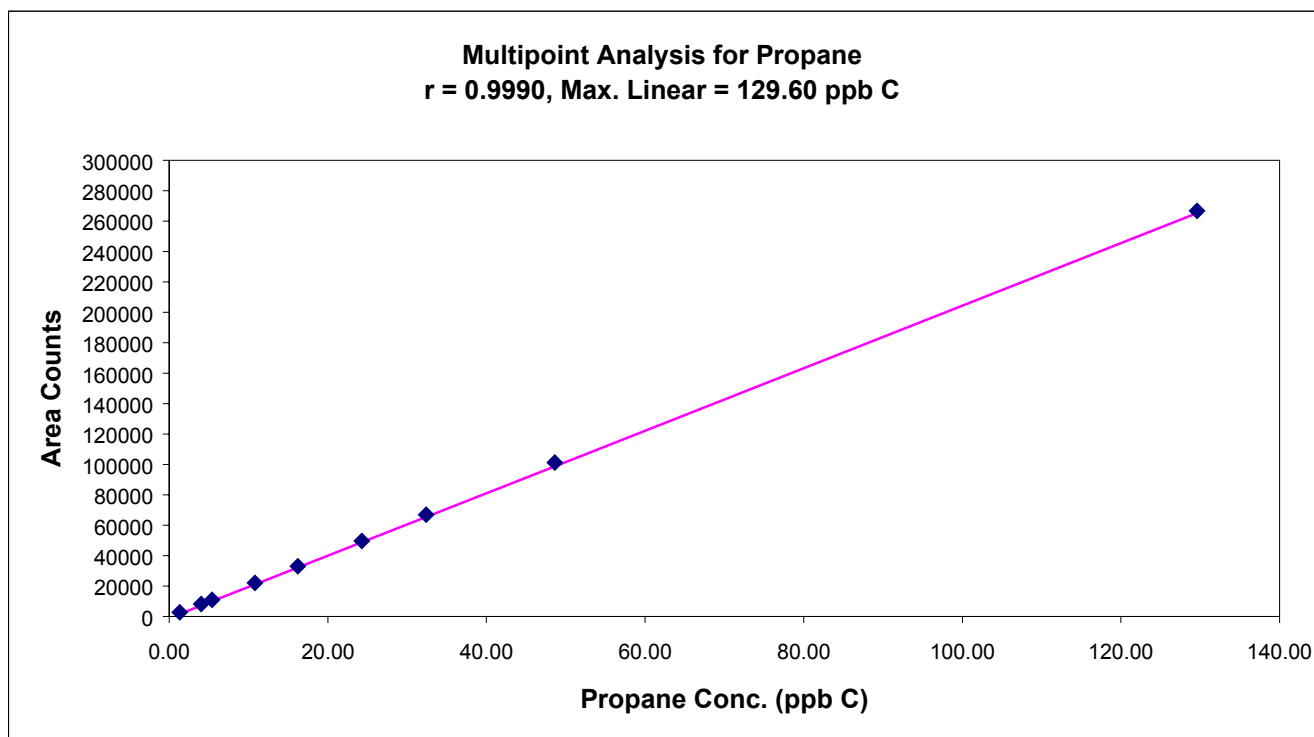
**Linear Regression Line:**

$$Y (\text{Area}) = a (\text{Area/Conc.}) * [X](\text{conc.}) + b (\text{Area})$$

**Regression Output:**

**Constant:** -1105.5 y-intercept, **b** (Area Counts)  
**Std Err. of Y Est:** 4139.3  
**No. of Observations:** 10  
**Degrees of Freedom:** 8  
**X Coefficient(s):** 2073.43 slope, **a** (Area Counts/ppb C)  
**Std. Err. of Coefficients:** 33.50  
**R Correlation Coefficient:** 0.99896

**Table 5A (Continuation). Multipoint Calculations for Propane**  
 Certified at 16.20<sub>ppb C</sub> - April 27, 1998



**Table 5B. LOD Calculations for Propane**  
 US EPA Method TO-15

SRM 1800-14-A (Propane)	Area Counts
[Propane] = 1.40 ppb C	2800
Rf = 0.0005 (ppb C/Mean)	2773
Degrees Of Freedom = 7	2758
t <sub>(n-1, Conf. = 99%)</sub> = 3.143	2786
	2840
	2877
	2770
Mean (Area Counts)	2800.6
Std (Area Counts)	43.04
Calc. LOD 3.143*Std*Rf	0.07 ppb C

**Table 6A. Multipoint Calculations for Benzene**  
 Certified at 31.20<sub>ppb C</sub> - April 27, 1998

**NIST Cylinder Number ALM033762 – SRM 1800-14-A**

Vol. sccm [ X ] <sub>ppb C</sub>	25 2.6	75 7.8	100 10.4	200 20.80	300 31.20	450 46.8	600 62.4	900 93.6	2400 249.6
Area Counts-FID	Area	Area	Area	Area	Area	Area	Area	Area	Area
1 <sup>st</sup> Run	5028	15918	21823	43558	64952	98965	133252	203350	545543
2 <sup>nd</sup>	5273	15997	21427	44579	65230	99269	133380	204543	545811
3 <sup>rd</sup>	5112	16030	21514	43557	64997	99230	133685	204756	545788
4 <sup>th</sup>	5238	16041	21474	43804	65227	99355	133465	205032	
5 <sup>th</sup>	5072				65744				
6 <sup>th</sup>	5218								
7 <sup>th</sup>	5248								
[Mean] <sub>ppb C</sub>	5170	15997	21560	43875	65230	99205	133446	204458	545714
[Std] <sub>ppb C</sub>	97.3	55.6	179.2	483.8	314.6	168.1	182.1	668.2	148.2
%RSD	1.88	0.35	0.83	1.10	0.48	0.17	0.14	0.33	0.03
# of Observations	7	4	4	4	5	4	4	4	3

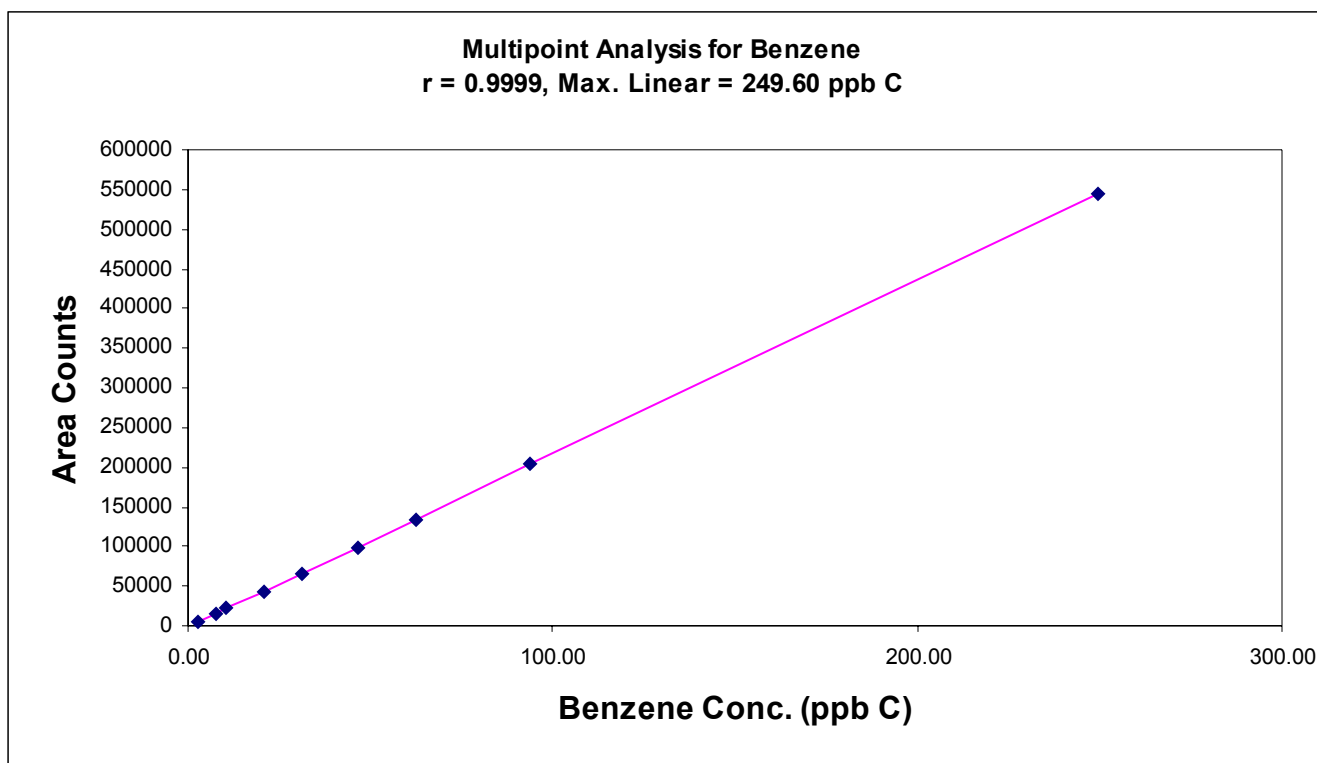
**Linear Regression Line:**

$$Y (\text{Area}) = a (\text{Area/Conc.}) * [X](\text{conc.}) + b (\text{Area})$$

**Regression Output:**

**Constant:** -1876.8 y-intercept, **b** (Area Counts)  
**Std Err. of Y Est:** 1216.2  
**No. of Observations:** 9  
**Degrees of Freedom:** 7  
**X Coefficient(s):** 2192.51 slope, **a** (Area Counts/ppb C)  
**Std. Err. of Coefficients:** 5.55  
**R Correlation Coefficient:** 0.99998

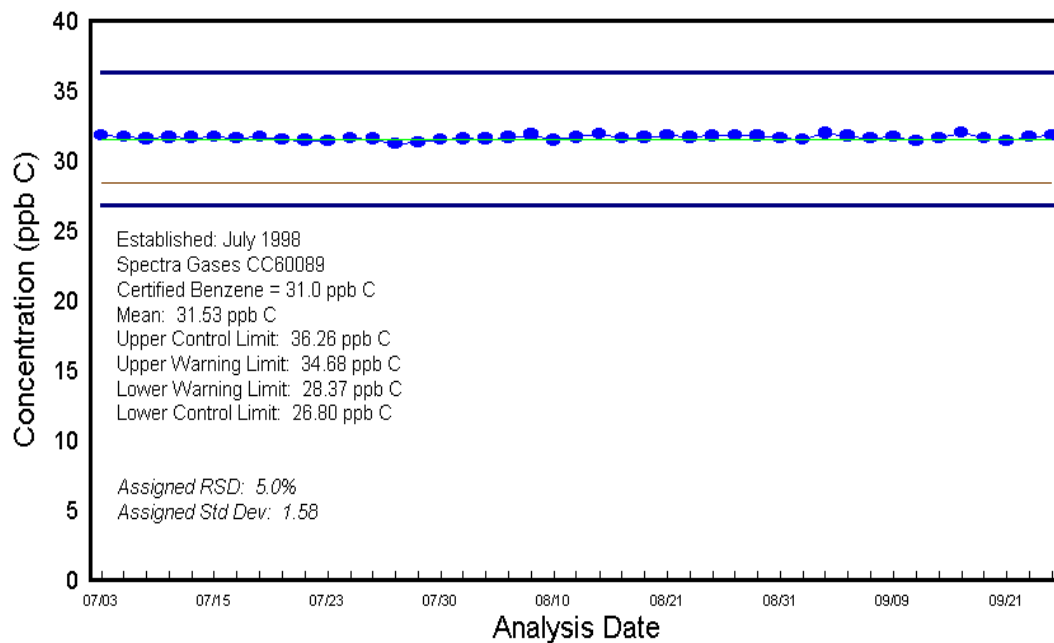
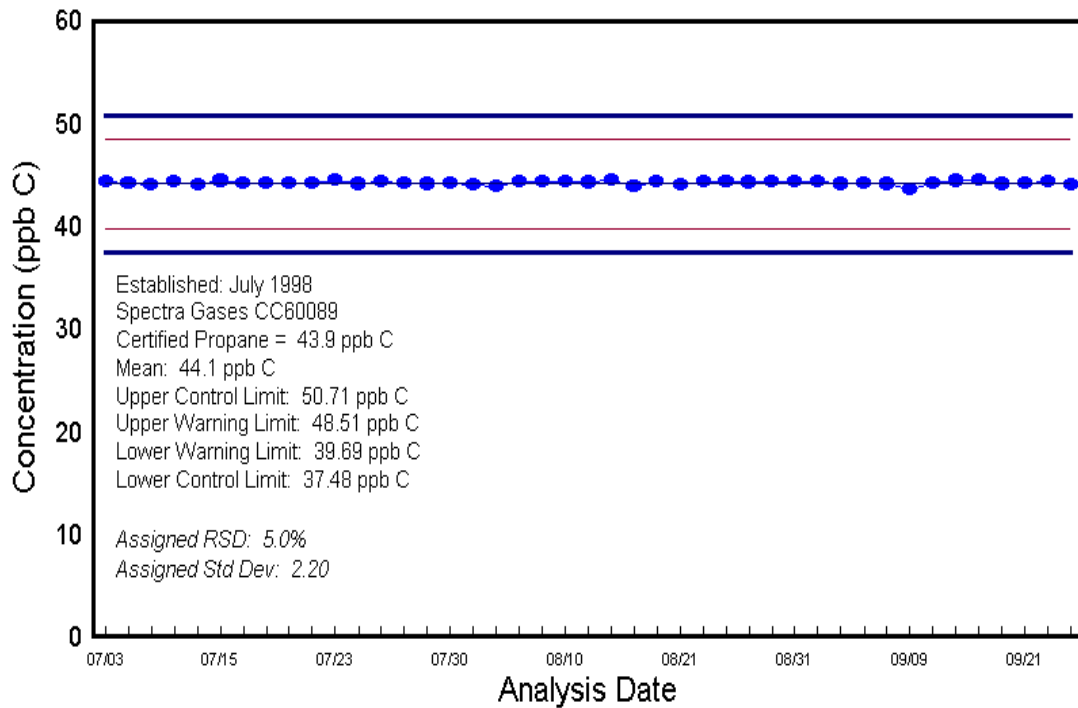
**Table 6A (Continuation). Multipoint Calculations for Benzene**  
 Certified at 31.20<sub>ppb C</sub> - April 27, 1998



**Table 6B. LOD Calculations for Benzene**  
 US EPA Method TO-15

SRM 1800-14-A (Benzene)	Area Counts
[Benzene] = 2.60 ppb C	5028
Rf = 0.0005 (ppb C/Mean)	5273
Degrees Of Freedom = 7	5112
$t_{(n-1, \text{Conf.} = 99\%)} = 3.143$	5238
	5072
	5218
	5248
Mean (Area Counts)	5169.8
Std (Area Counts)	97.26
Calc. LOD $3.143 \times \text{Std} \times \text{Rf}$	<b>0.15 ppb C</b>

**Table 7. Control Charts for Propane and Benzene**



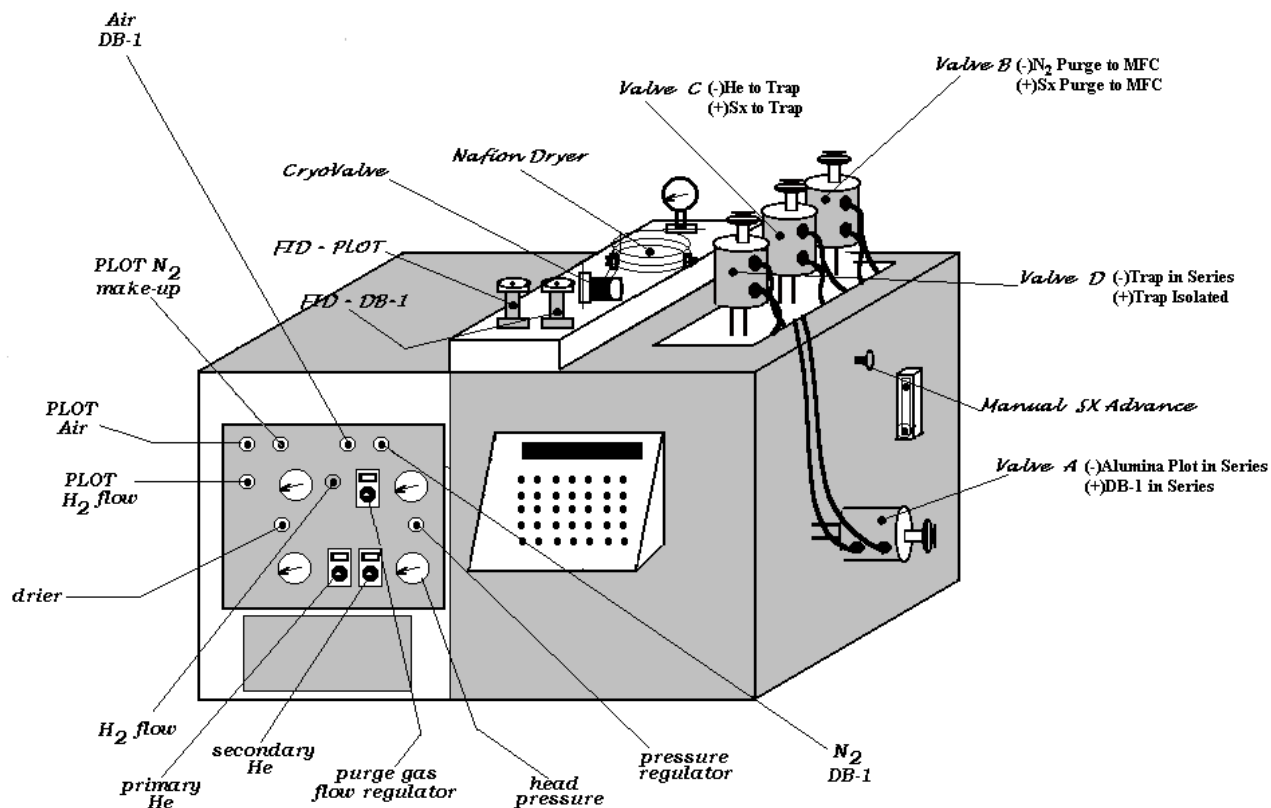
**Figure 1. Varian 3600Cx GC Analytical System**

**MLD032 - NMOC Speciated VOC Analysis**









**Figure 2A. Pre-Injection Time Events**

Pre-injection system configuration: Time = 0.00min

\* Normal operation - All valves are off, ( )

\* MFC sampling

\* Ready/Standby Position

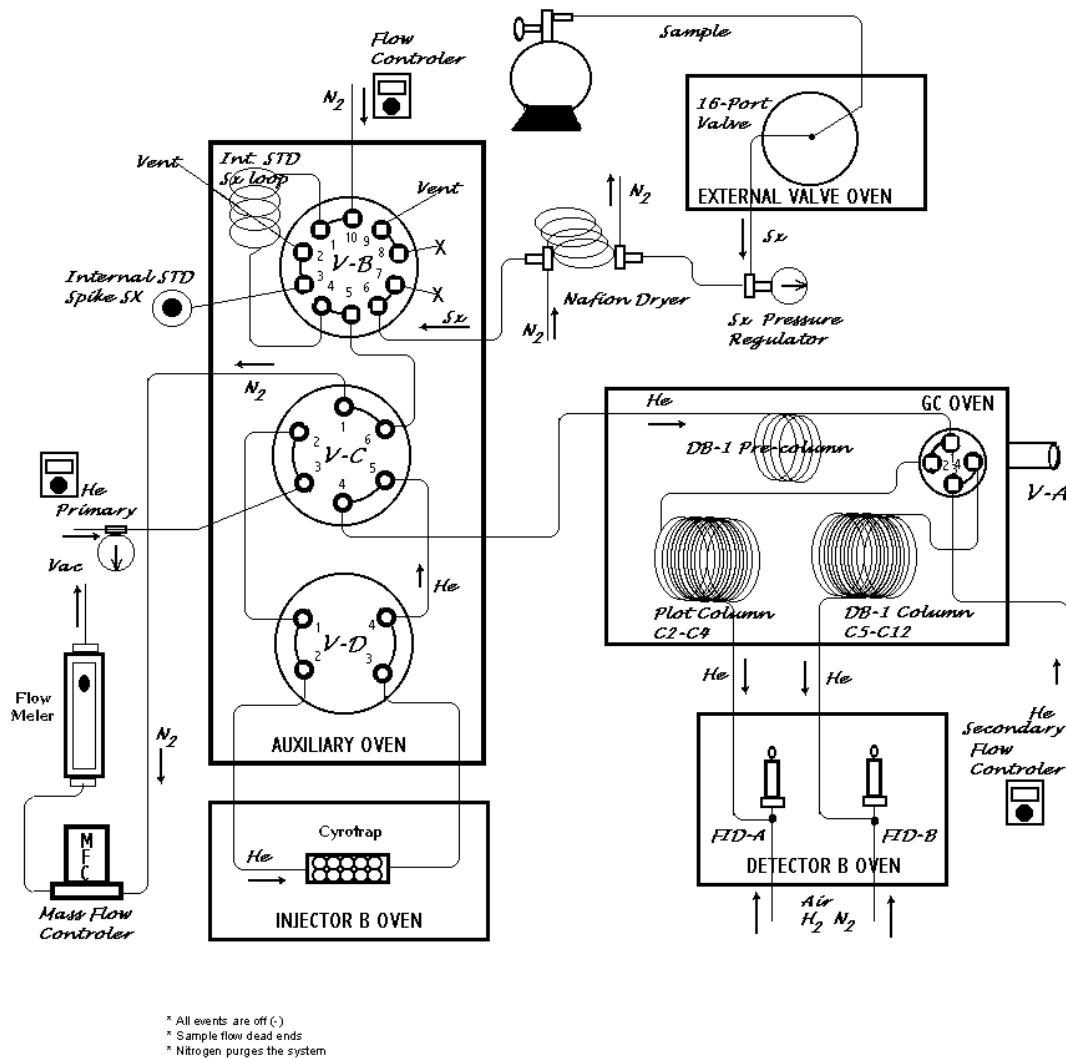
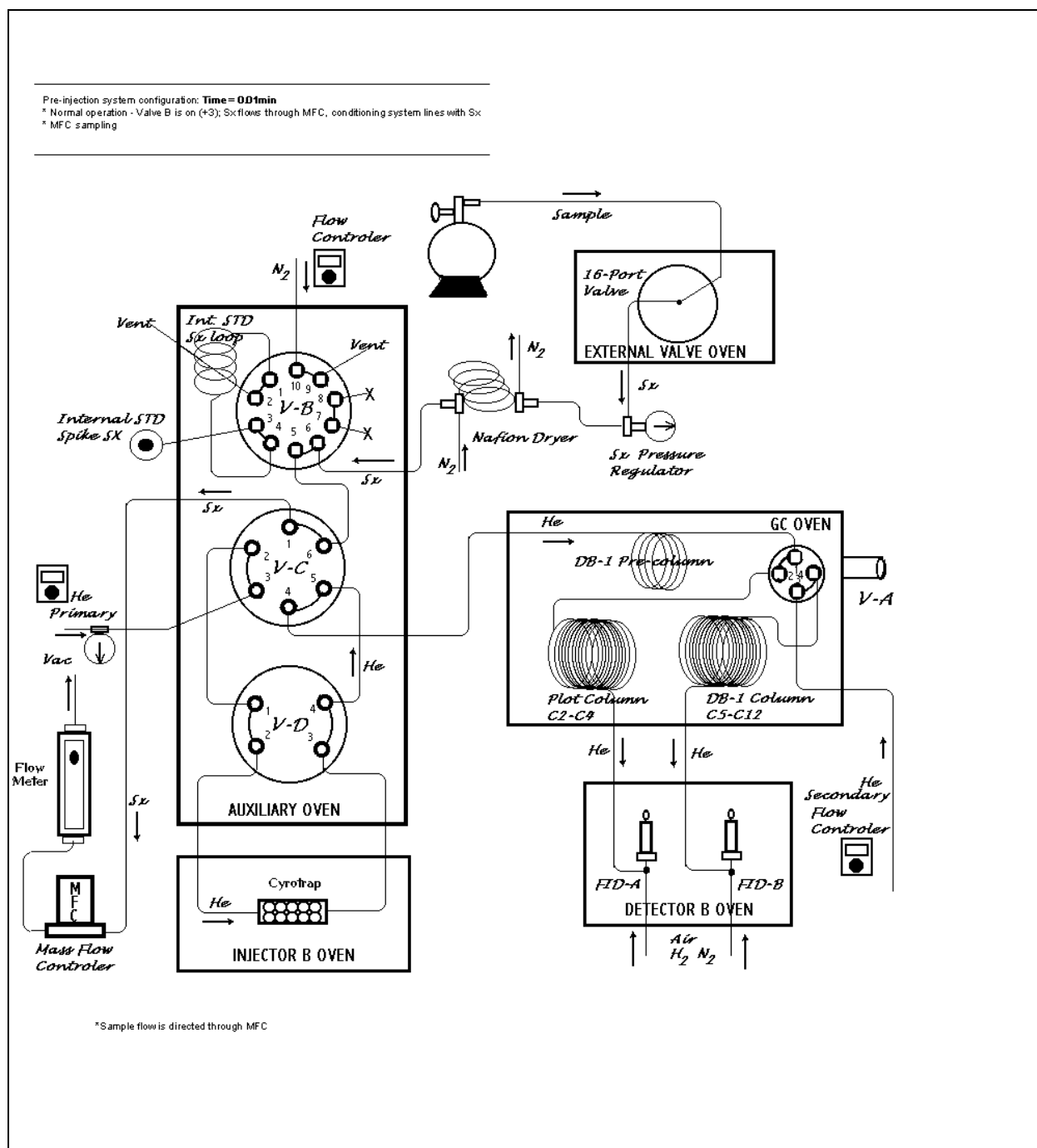


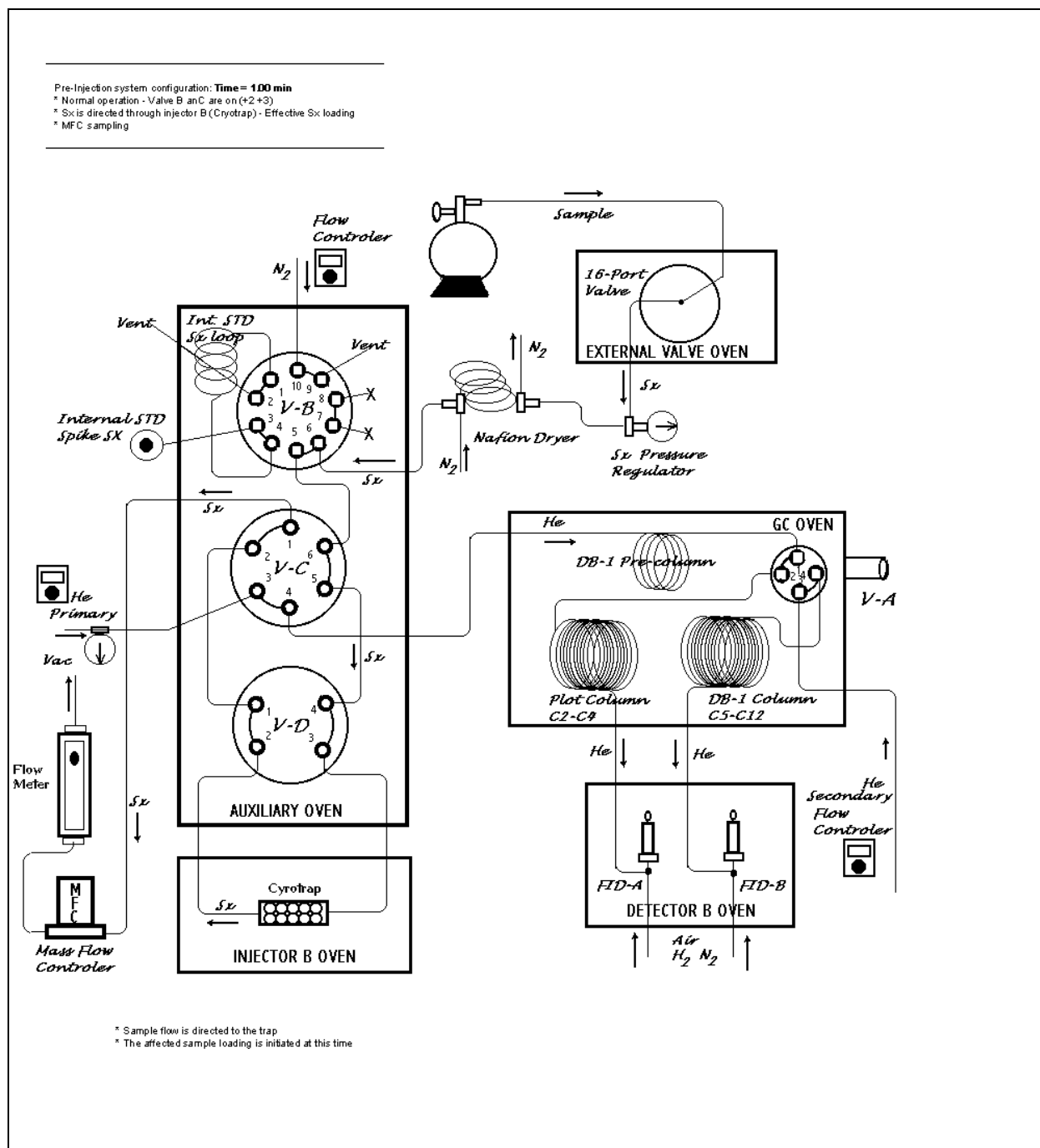
Figure 2A: Time: 0.00 min –All events are off

**Figure 2B. Pre-Injection Time Events**



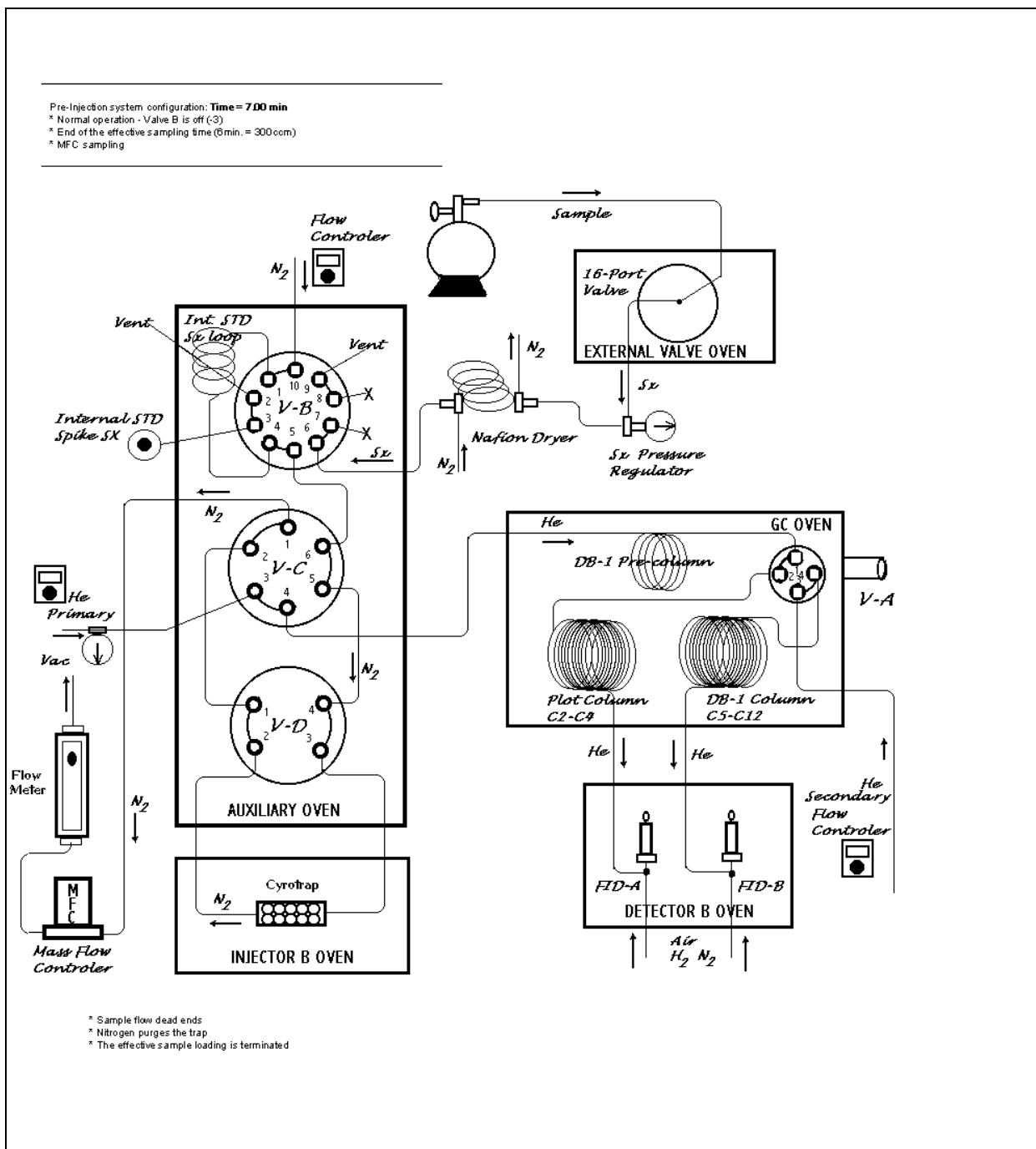
**Figure 2B: Time: 0.01 min –Valve B is on (+3)**

**Figure 2C. Pre-Injection Time Events**



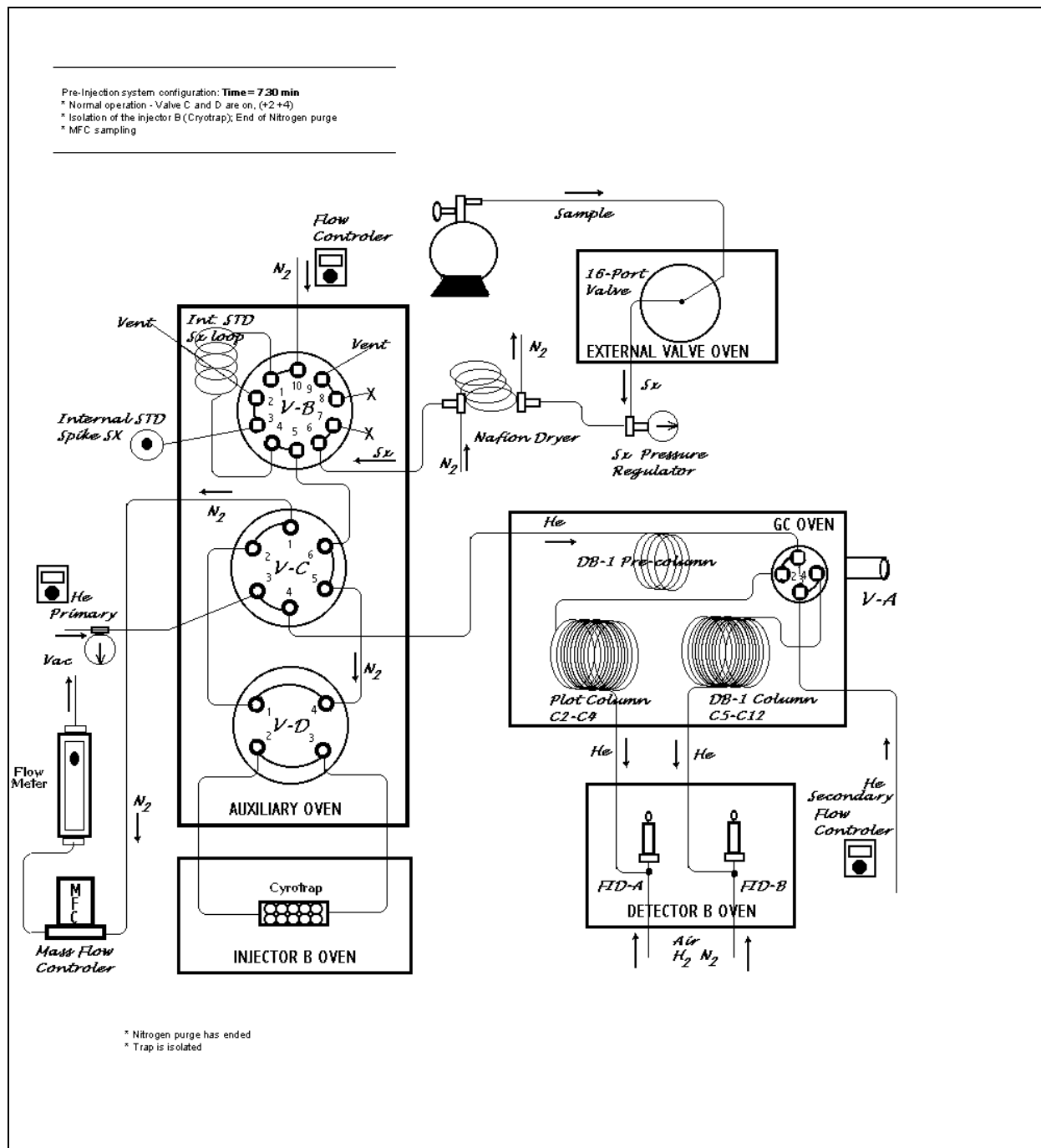
**Figure 2C: Time: 1.00 min –Valves B and C are on (+2 +3), effective sample loading.**

**Figure 2D. Pre-Injection Time Events**



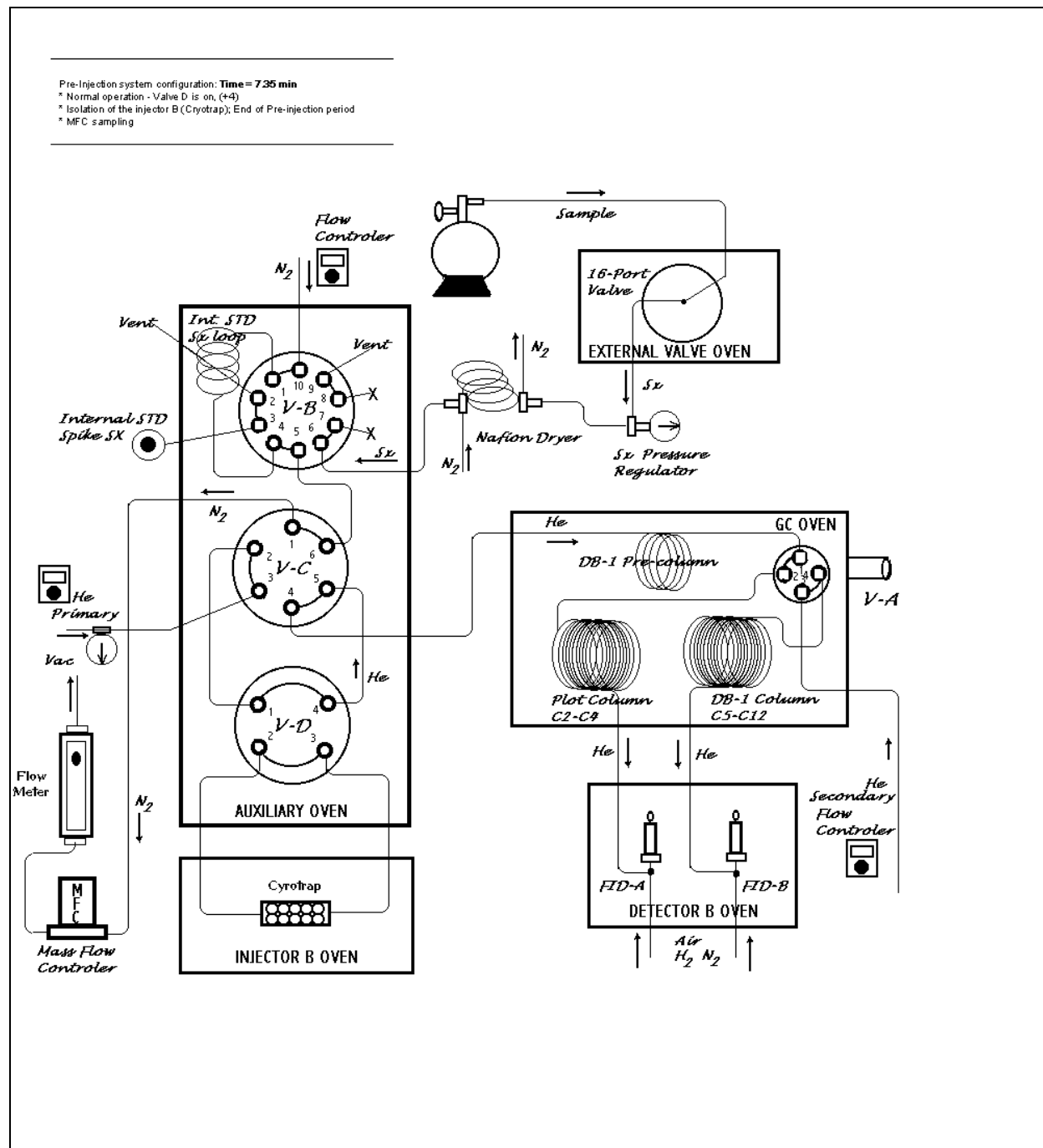
**Figure 2D: Time: 7.00 min –Valve B is deactivated (-3), end of sampling period. The trap is purged with nitrogen.**

**Figure 2E. Pre-Injection Time Events**



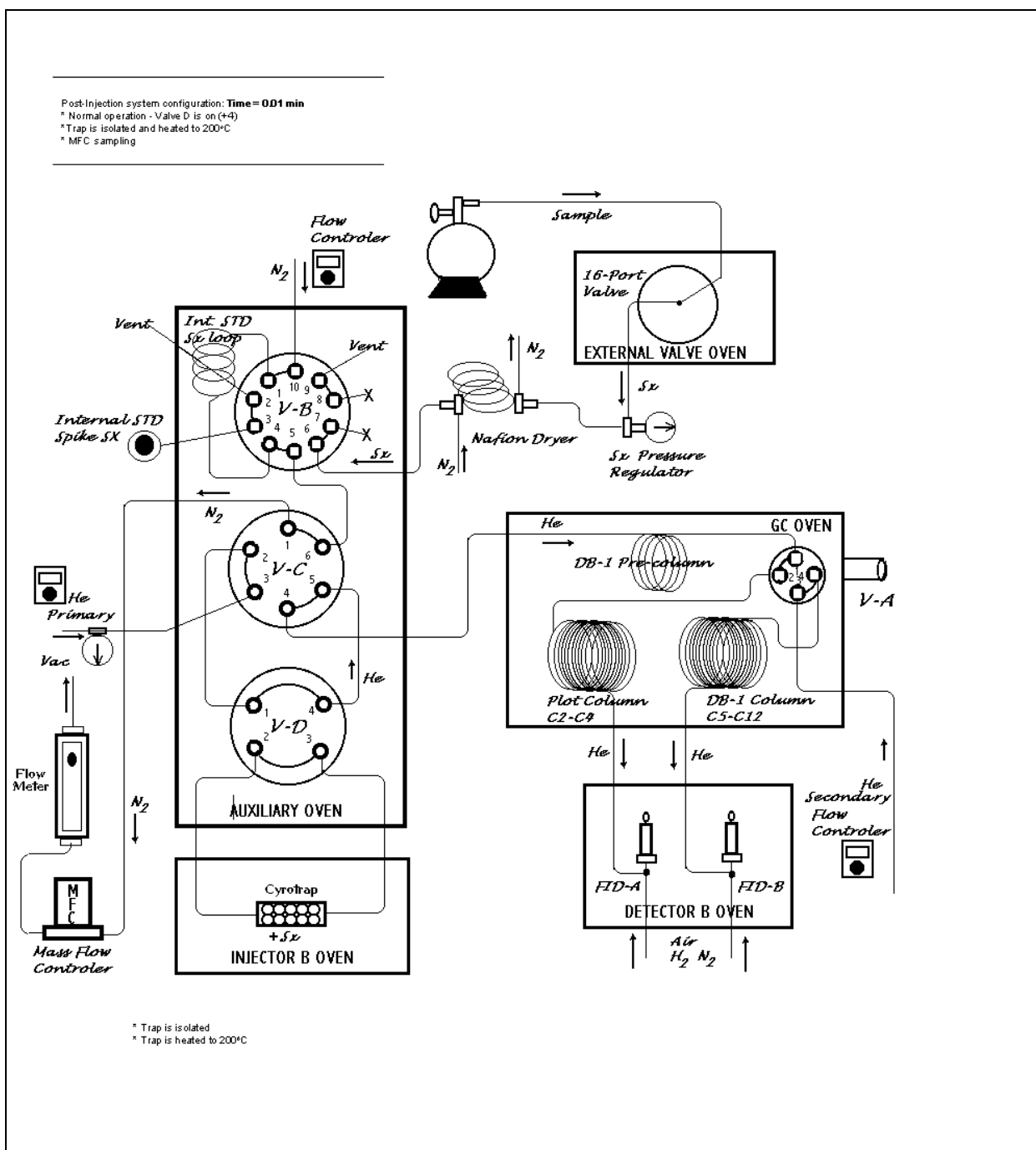
**Figure 2E: Time: 7.30 min –Valve B is off (-3), Valves C and D are on (+2 +4), end of nitrogen purge of the trap. The trap is isolated and ready for heating.**

**Figure 2F. Pre-Injection Time Events**



**Figure 2F: Time: 7.35 min –Valve C is off (-2), Valve D is on (+4), trap is still isolated and this is the end of pre-injection program.**

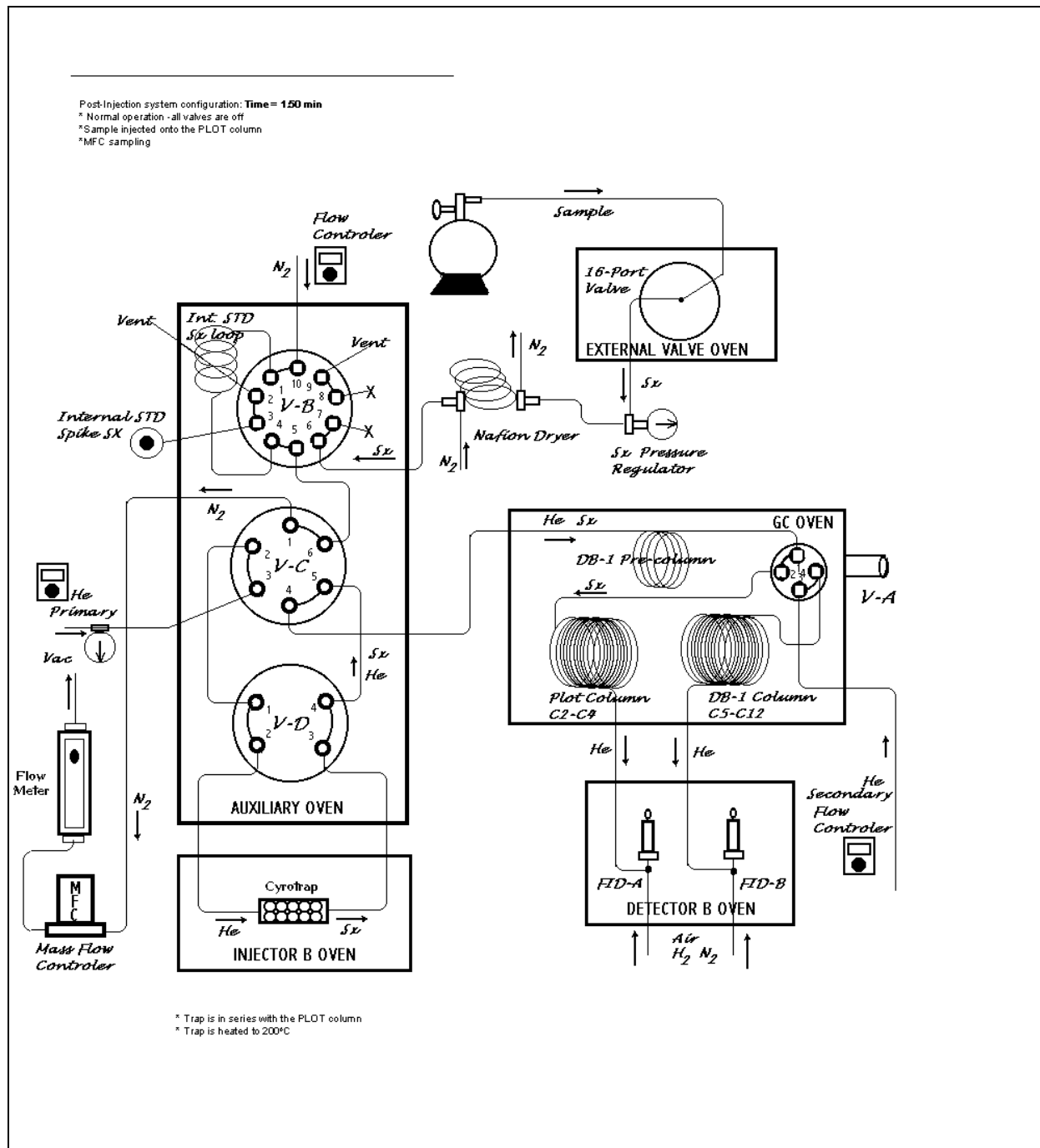
**Figure 3A. Post-Injection Time Events**



**Figure 3A: Time: 0.01 min –Valve D is on (+4), the trap is isolated and is being heated.**

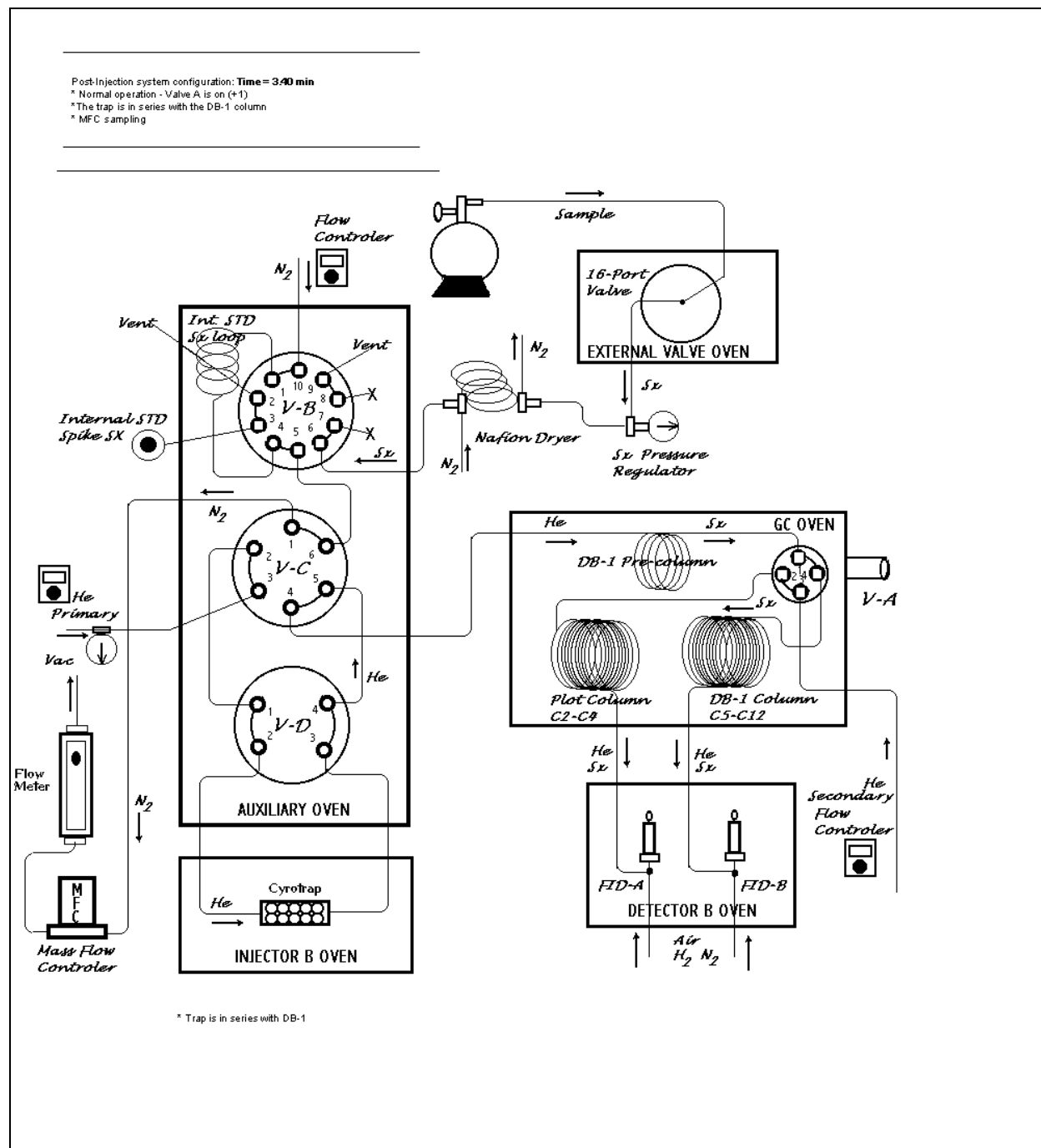


**Figure 3B. Post- Injection Time Events**



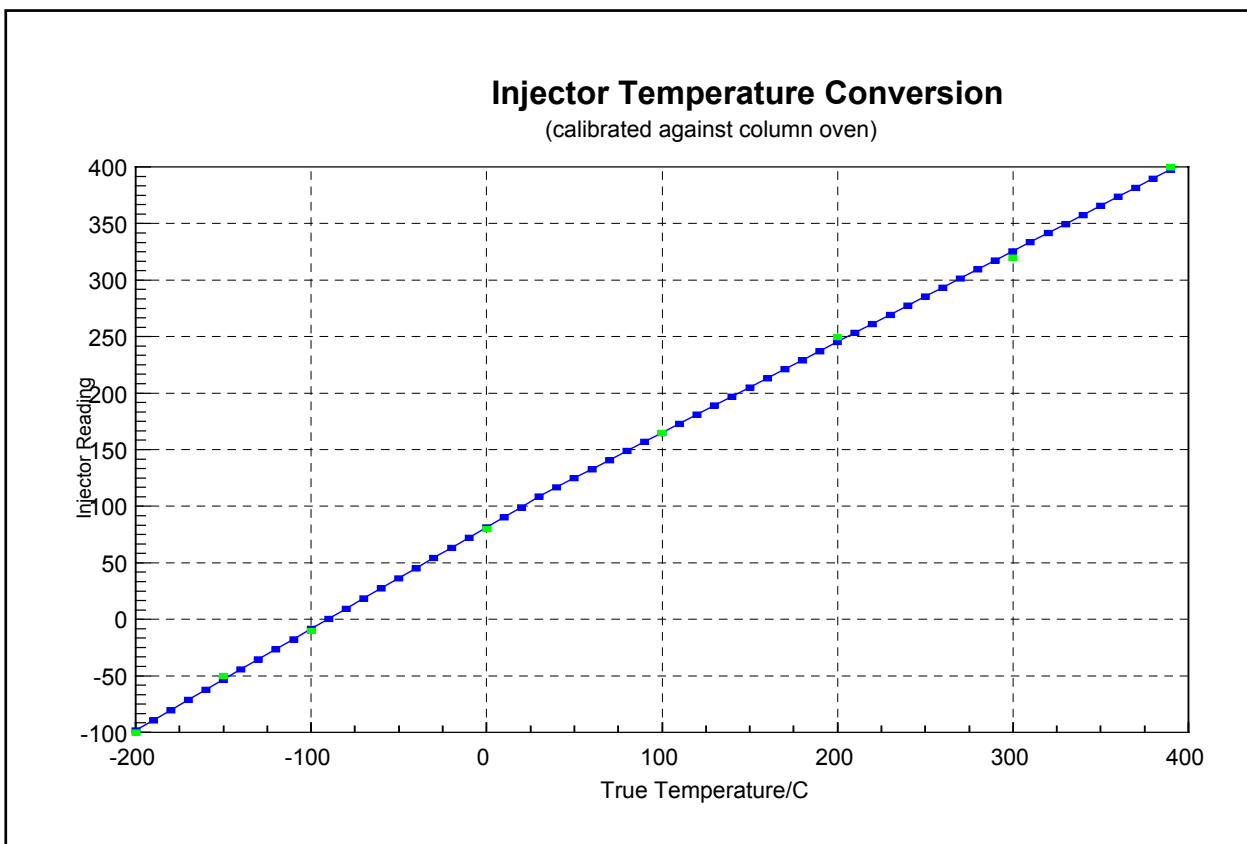
**Figure 3B: Time: 1.50 min –all Valves are off, sample is injected onto the PLOT column.**

**Figure 3C. Post-Injection Time Events**

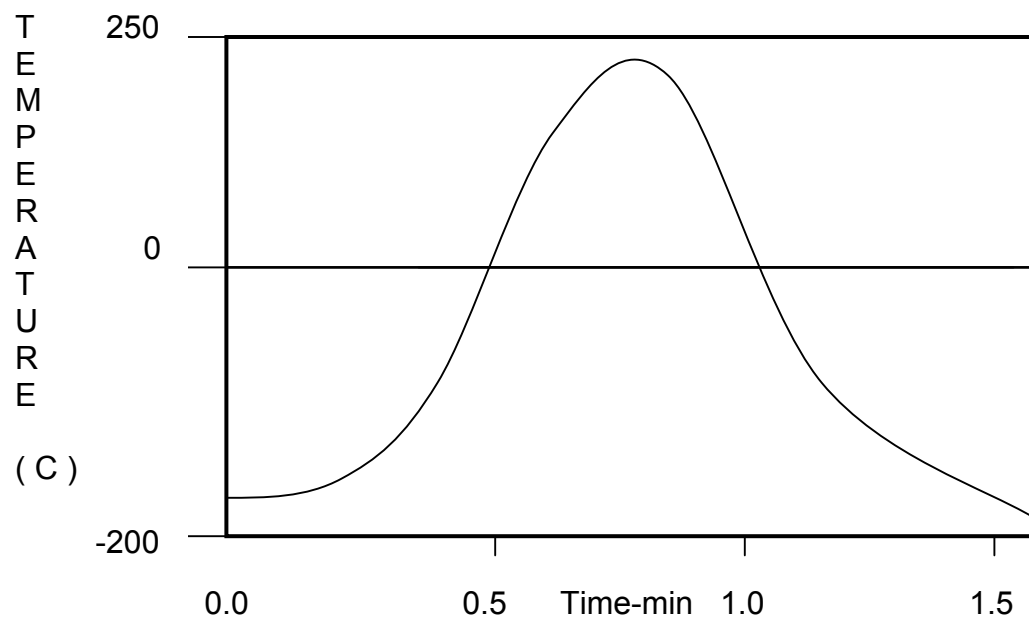


**Figure 3C: Time: 3.40 min –Valve A is on (+1), the sample is redirected onto the DB-1 column.**

**Figure 4. Injector B Temperature Conversion**

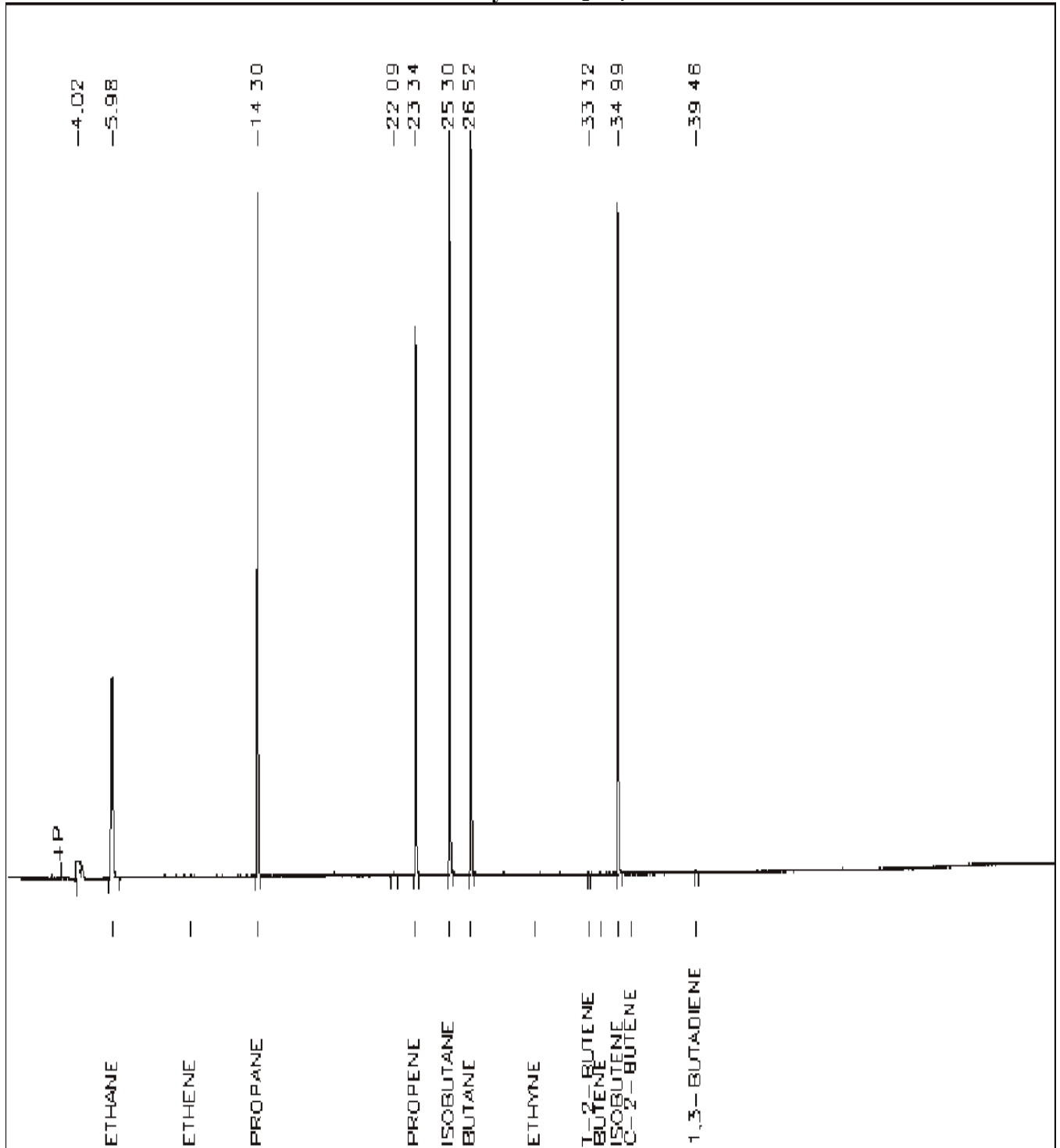


**Figure 5. Injector B Temperature Profile**



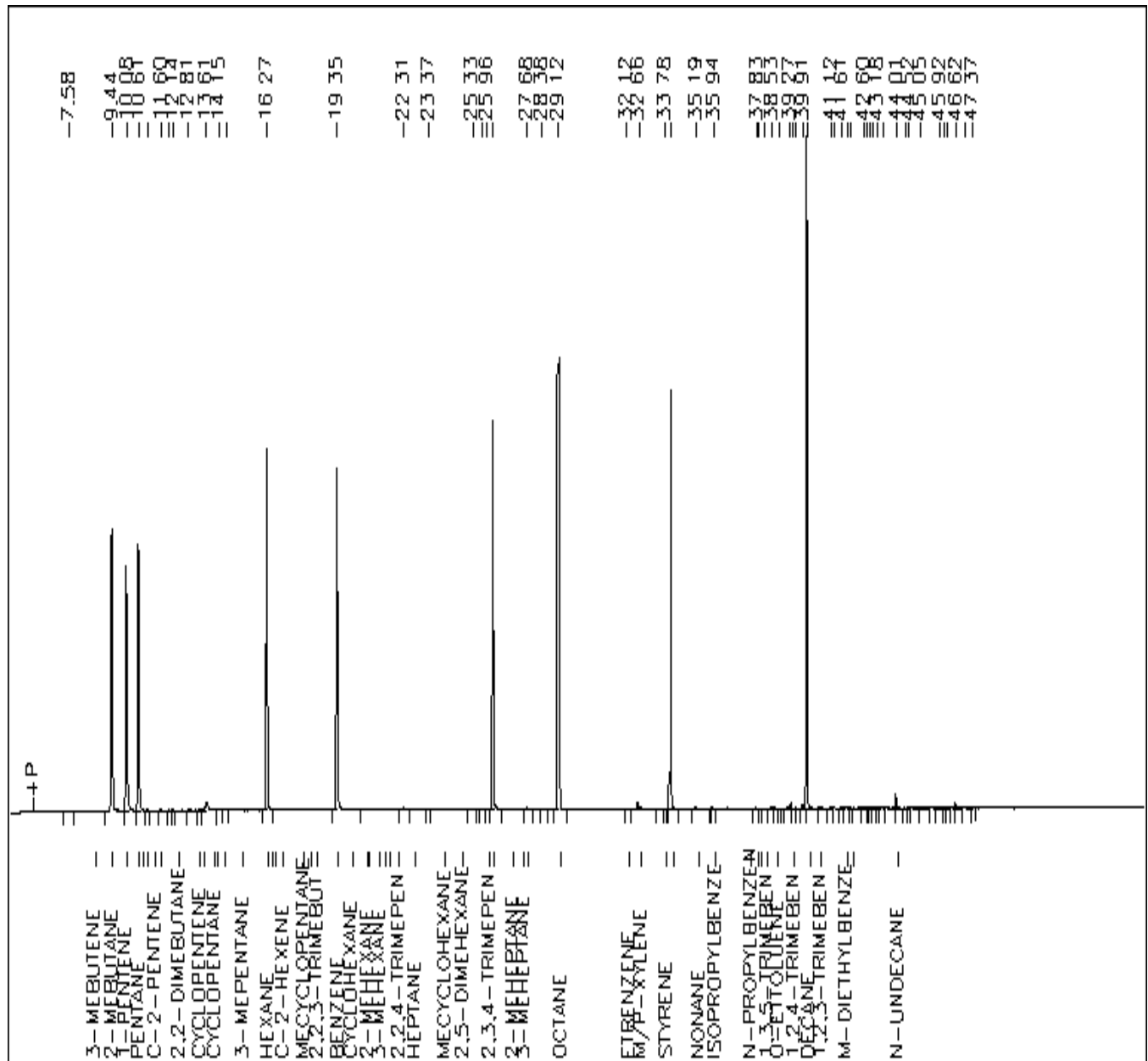
**Figure 6A. NIST SRM 1800 VOC Standard**

# PLOT Analysis of C<sub>2</sub>-C<sub>4</sub> VOCs

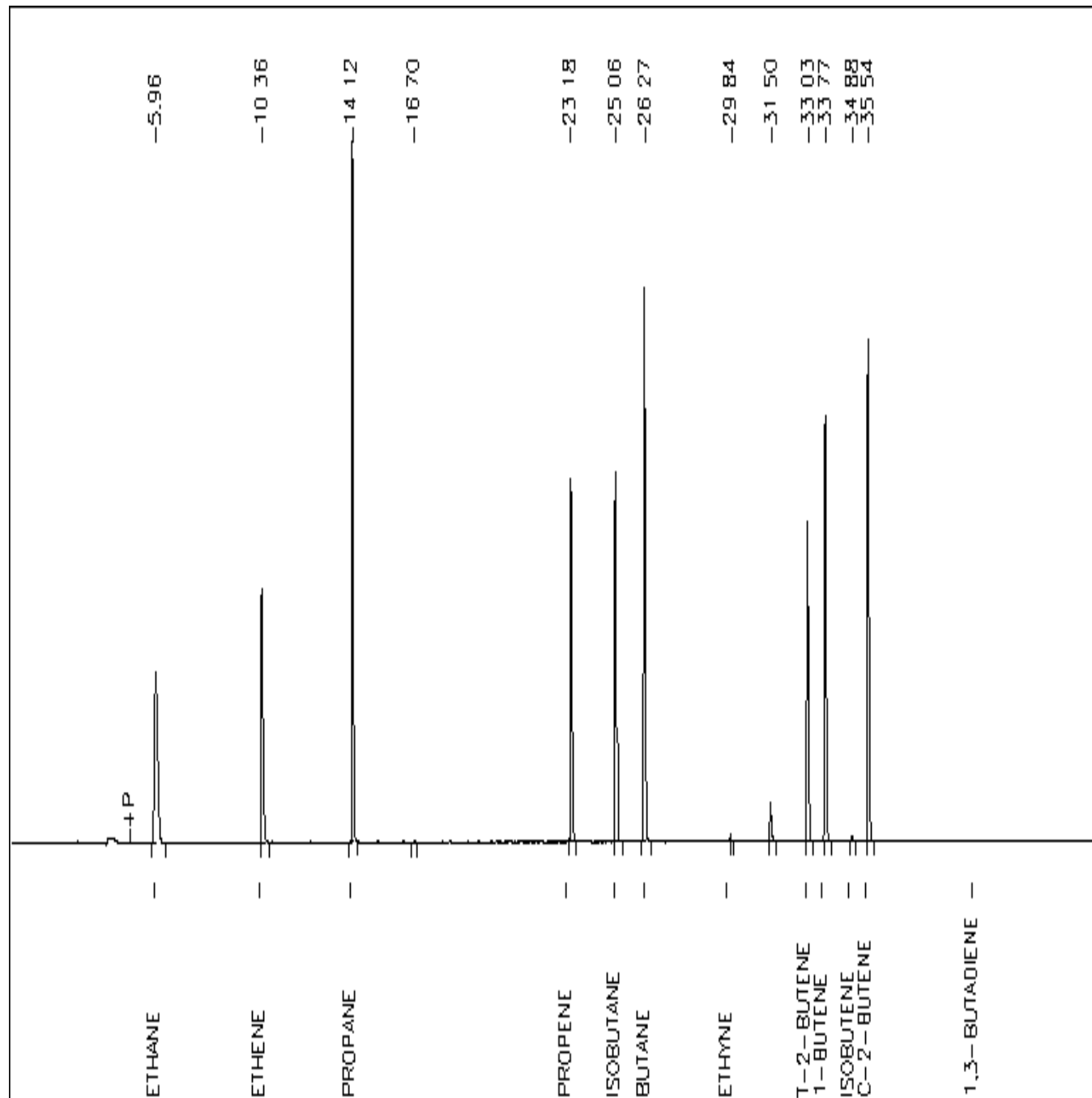


**Figure 6B. NIST SRM 1800 VOC Standard**

**DB-1 Analysis of C<sub>5</sub>-C<sub>10</sub> VOCs**

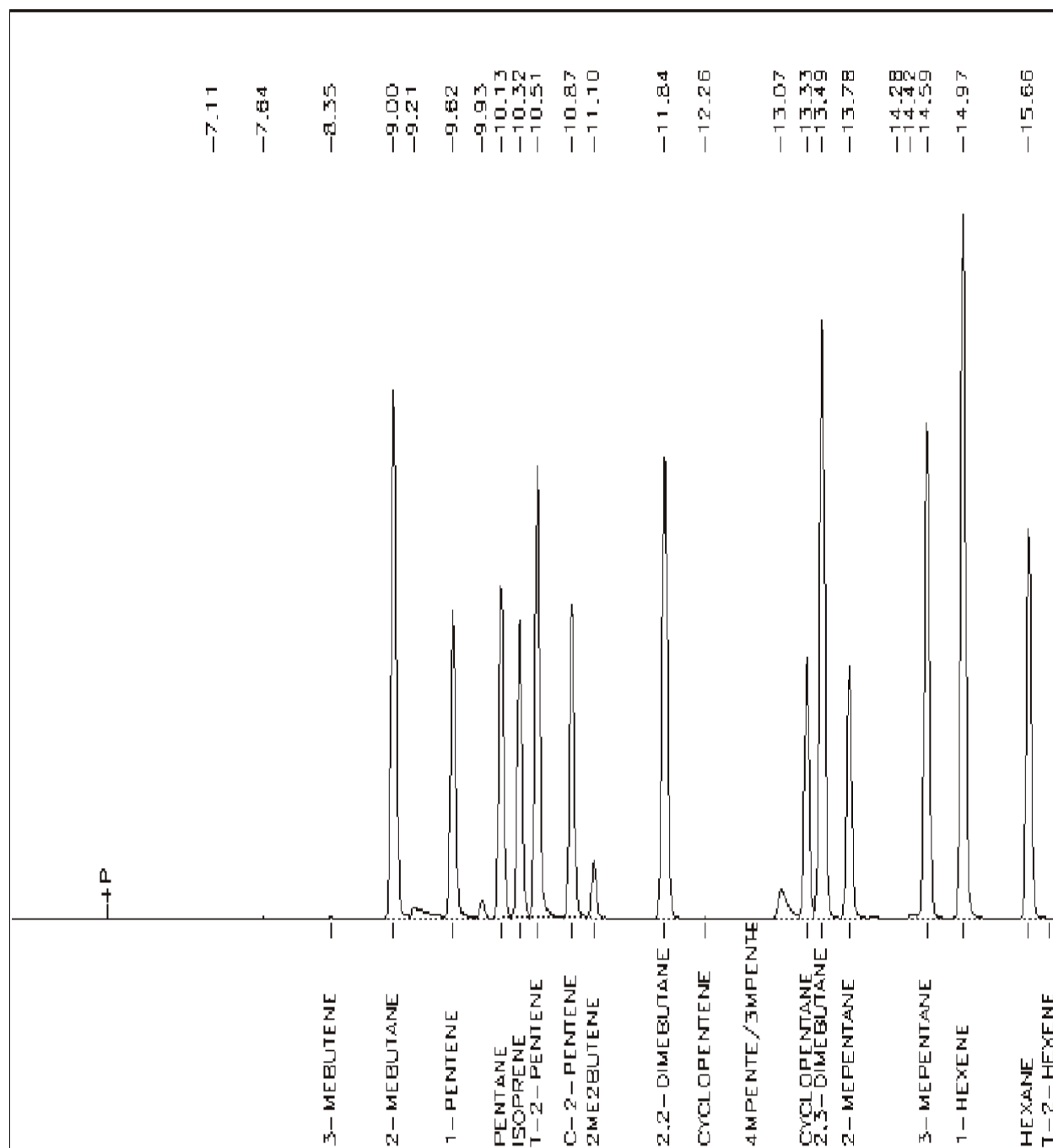


**Figure 7A. PAMS Retention Time Standard (CC60089)**  
**PLOT Analysis of C<sub>2</sub>-C<sub>4</sub>VOCs**



**Figure 7B. PAMS Retention Time Standard (CC60089)**

**DB-1 Analysis of C<sub>5</sub>-C<sub>12</sub> VOCs**

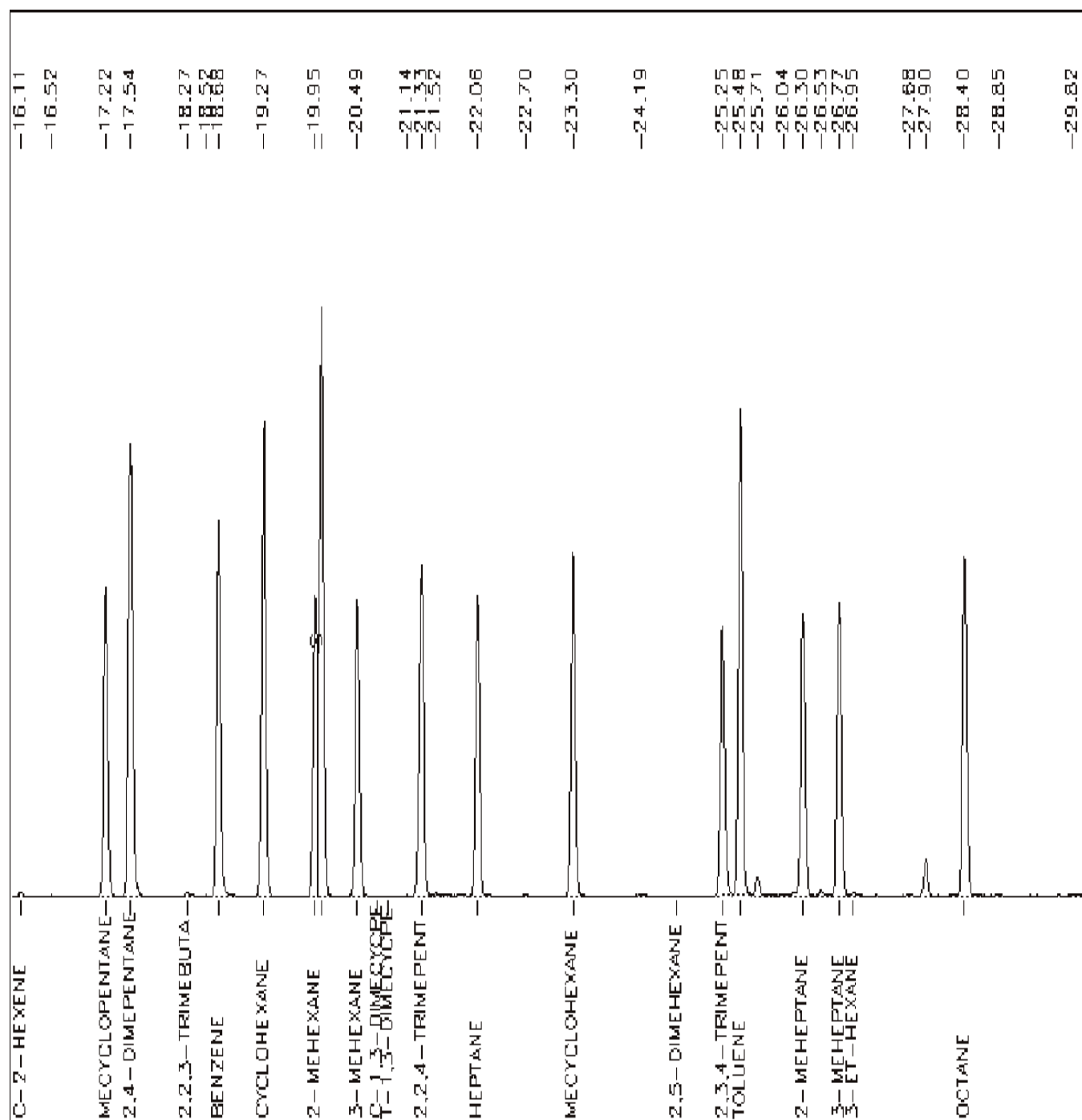




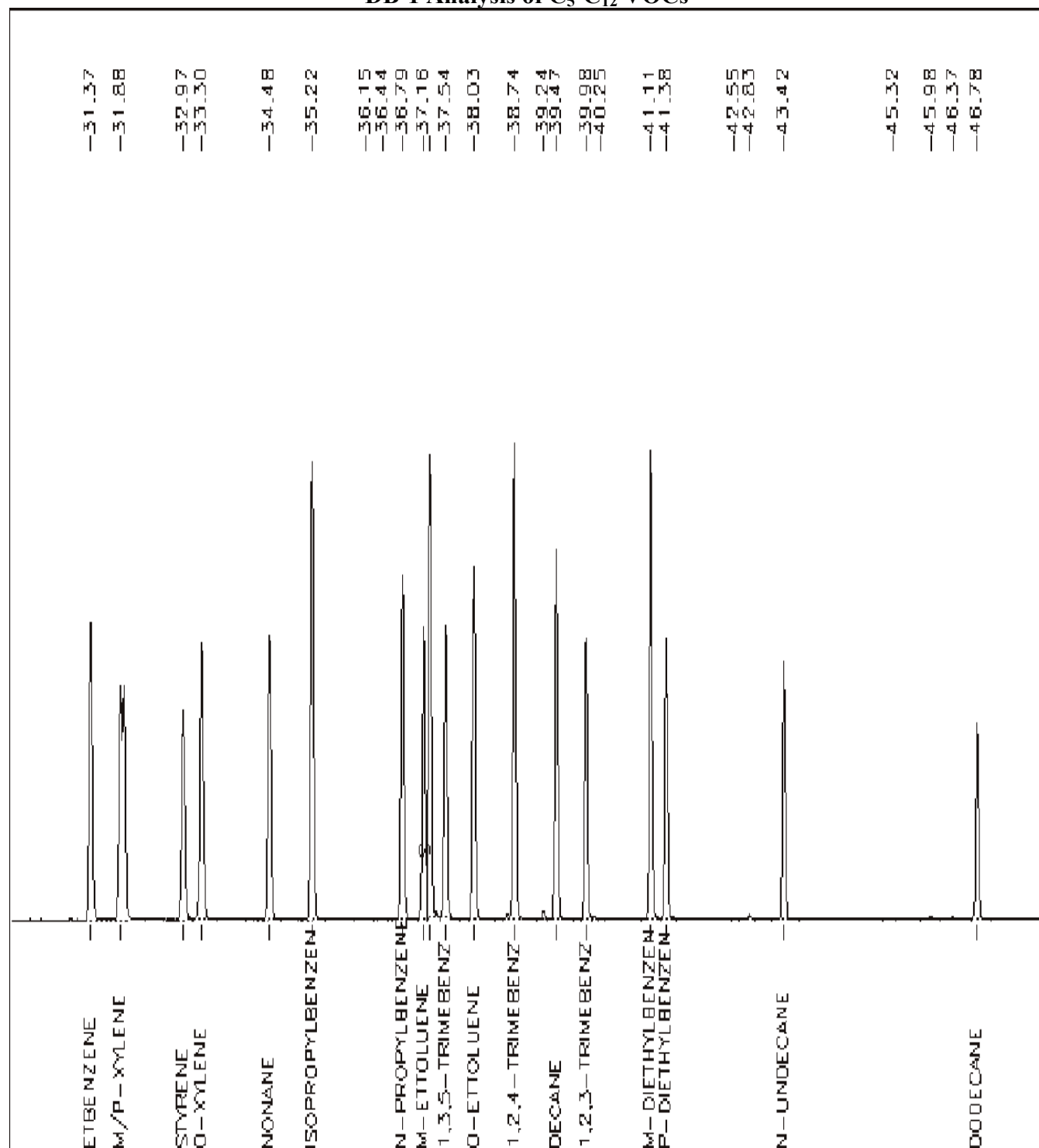
**Figure 7B. PAMS Retention Time Standard (CC60089)**

**DB-1 Analysis of C<sub>5</sub>-C<sub>12</sub> VOCs**





**Figure 7B. PAMS Retention Time Standard (CC60089)**  
**DB-1 Analysis of C<sub>5</sub>-C<sub>12</sub> VOCs**



## APPENDIX I

### Flow Rate Settings

GC Column Standby Temperature ----- 100 °C

#### He Carrier Gas (primary and auxiliary):

Set to  $5.00 \pm 0.3$  cm<sup>3</sup>/minute

Flow Controller (primary) ----- Set digital gauge at 5.55 (~ cm<sup>3</sup>/minute)

Flow Controller (auxiliary) ----- Set digital gauge at 5.05 (~ cm<sup>3</sup>/minute)

Pressure Regulator ----- Set analog gauge to 49.8 psi

#### N<sub>2</sub> Make-up Gas:

FID (DB-1) ----- Set N<sub>2</sub> flow to  $15 \pm 2.0$  cm<sup>3</sup>/minute

FID (PLOT) ----- Set N<sub>2</sub> flow to  $15 \pm 2.0$  cm<sup>3</sup>/minute

#### Air (Oxidant) Flow:

FID (DB-1) ----- Set Air flow to  $300 \pm 10$  cm<sup>3</sup>/minute

FID (PLOT) ----- Set Air flow to  $300 \pm 10$  cm<sup>3</sup>/minute

Total He, N<sub>2</sub> and Air Gas Flow ----- ~360 cm<sup>3</sup>/minute

#### N<sub>2</sub> Purge Gas:

Flow Controller ----- Set digital gauge at 57.5 (~ cm<sup>3</sup>/minute)

N<sub>2</sub> purge Pressure Gauge ----- Reads > 60 psi

N<sub>2</sub> Nafion<sup>TM</sup> Counterflow ----- Set to ~200 cm<sup>3</sup>/minute (min. 3X Sx flow)

#### Mass Flow Controller (MFC):

Set sampling flow rate to 50 cm<sup>3</sup>/minute

Set ----- 50.0% of full scale

Read ----- 50.0% of full scale

----- 100 cm<sup>3</sup>/minute equals 100% full scale

#### Required Regulator Pressures:

He - Carrier Gas ----- 80 psi

He - Valve Actuator Gas -----  $\geq 65$  psi

N<sub>2</sub> - Make-up Gas----- 80 psi

N<sub>2</sub> – Dryer Purge Gas ----- 80 psi

## APPENDIX II

### TURBOCHROM – PE NELSON 2700 DATA SYSTEM

TURBOCHROM CHROMATOGRAPHY SYSTEM by PE Nelson: Turbochrom (Ver. 4.1) is a Microsoft Windows spreadsheet driven system. Here is a brief explanation of NMOC speciated chromatography setup for acquiring data, report formats, editing calibration methods, editing sequence files, incorporating Rf's, batch reprocessing the raw data files and creating peak summary reports.

The Navigator window is a graphical representation of the major functions in Turbochrom. The icons and menus along with their respective functions are as follows:

#### BUILD

- Method** This is where you can edit (non-graphically) the calibrating as well as acquiring method for any GC instrument.
- Sequence Build** This is where you can edit or build sequences.
- Graphic Edit** This allows you to graphically edit methods using a \*.raw file.

#### ANALYSIS

- Setup** In this window you can edit the setup of the instruments, including the sequence and method files used and where created data files are stored.
- Hands On** This allows you to control instrument settings.

#### VIEW

- Modify** Here you can modify the active sequence or active method.
- Details** Lets you view detailed information about every instrument configured on your system.
- Status** Shows the current status of every instrument configured on your system.
- Real-Time Plot** This option allows you to view data points in real time.

## REPROCESS

<b>Results</b>	Allows you to reprocess *.raw data files with the calibrating method.
<b>Batch</b>	Allows you to reprocess a number of *.raw data files at a time with the calibrating method.
<b>Summary</b>	Here you can create a report which summarizes the results for an entire sequence by component.

## DISPLAY

<b>Chromatograms</b>	This option allows you to view multiple chromatograms and do overlays or other comparisons.
<b>Spectra</b>	This is not used.

## MENUS

<b>Run Menu</b>	This controls single or multiple runs.
<b>App. Menu</b>	Here you can access any add-on applications, such as TC2ASCII.
<b>Help Menu</b>	Allows you to get help for Turbochrom.
<b>Instruments</b>	The instruments panel lists the instruments configured on the system. In our case there are three instruments listed: Instrument_ <b>B</b> (HC16) Instrument_ <b>C</b> (HC20) Instrument_ <b>D</b> (HC22)

## INSTRUMENT

There are presently three instruments that are configured with PE Nelson 2700 Chromatography system: Instrument\_ **B** (HC16), Instrument\_ **C** (HC20), and Instrument\_ **D** (HC22).

System configuration is performed in the Configuration window (Config Icon), which allows you to edit the **F**ile menu (edit default printer), **C**olors command (defines colors



for various screens), Instrument command (edit configuration of all instruments connected to the computer), **Path** menu(define where the data, methods and sequence can be stored), and **Options** menu (preferences in Graphic Method Editor, initialization of any 900 Series Interface). The Configuration summary for the GC instruments in the PC is as follows:

<u>Instr. No.</u>	<u>IEEE Add.</u>	<u>Instr. Type</u>	<u>Instr. Name</u>	<u>Autosampler Type</u>
1	0	PEN900	Instr._ <b>B</b> _HC16	None
2	1	PEN900	Instr._ <b>C</b> _HC20	None
3	2	PEN900	Instr._ <b>D</b> _HC22	None

There are three types of paths configured for each instrument: **1. System path** - path names of the directories that Turbochrom searches to find method (\*.mth) and sequence (\*.seq) files; **2. Program path** - drive and directory where the configuration, program, and library files are located; **3. Component defaults path** - DEFAULT.CMP file that contains default values that Turbochrom uses for editing new components to the method. Currently, paths configuration for the three instruments are set as follows:

Program Path	C:\TC4-2f12
System Path 1	C:\TC4-2f12\data16
System Path 2	C:\TC4-2f12\data20
System Path 3	C:\TC4-2f12\data22
Component defaults path	C:\TC4-2f12

### **FILE NAME FORMAT**

The Nelson 2700 system (Turbochrom) uses 8 characters to form the file base name, three of which are reserved for numbering the data files and one for appending the duplicate analysis. By default, one can edit the **MMDD\*\*\*\*** (i.e., **JN12**), where Turbochrom will append the cycle number and a letter for duplicate analysis **MMDD\*\*\*\*** (i.e., **001a**). To ensure that the base file name is unique and is indicative of the instrument that is generating the raw data file, 5 characters are used to form the file base name. The cycle of injection number is appended to the selected base name manually and the data files are stored on the specified drive and subdirectory. The same base name is used for storing raw (\*.raw) and

result (\*.rst) files, where the three character extension differentiates one file from another. If a duplicate file name exists, a lower case "a" will be automatically

appended to the cycle of injection number and will distinguish the file as being a second analytical run for the same sample in the sequence. To prevent any confusion and to allow easy identification of data, the following naming convention is used:

1. Use only a 5 character base name for data runs.
2. The first two characters will be a month code.
3. The third and fourth characters will be a date code.
4. The fifth character will be an instrument code: B, C, D.
5. The sixth through ninth character is manually assigned by the operator and represents the sample number for the base name.

<u>MONTH CODES</u>		<u>INSTRUMENT CODES</u>
JAN = <b>JA</b>	JUL = <b>JL</b>	METHOD 002 = <b>A</b>
FEB = <b>FB</b>	AUG = <b>AU</b>	METHOD 012 = <b>Z</b>
MAR= <b>MR</b>	SEP = <b>SE</b>	METHOD 013 = <b>D</b>
APR = <b>AP</b>	OCT = <b>OC</b>	METHOD 032 = <b>B/C/D</b> (3 instruments)
MAY= <b>MY</b>	NOV = <b>NO</b>	
JUN = <b>JN</b>	DEC = <b>DE</b>	

**EXAMPLE:** **SE08D004** Would be September 8th - Instrument HC22, Method MLD032 Speciated NMOC Analysis, cycle/injection number 4.

#### **SAMPLE NAME FORMAT:**

Within a sequence or during a manual download you must enter a sample name. The format for this is as follows:

- \* Generally a system blank or a sample of Grade 5 Nitrogen or equivalent is run as the first sample of the day to insure that the system is free of contamination.
- \* Enter system blank as: **BLK**

\* The calibration NIST SRM1800 standard (ALM033762) with certified values for propane and benzene is run, labeled: **STD33762**

\* The 15 component retention time standard that validates the calibration of the instruments is run, and is labeled: **CTL60089**

Once samples have been logged into LIMS, their corresponding data will be updated and transferred. A sample is identified in LIMS as being part of the NMOC analysis by the first 2 characters (i.e., **NM**) of the sample name. The rest of the LIMS numbers will be limited to 6 characters and the 7th character is used as a replicate code. If this is left blank, it represents the first analysis. A-J represents the 1st through 9th replicates. For example, if the LIMS number is **NM000125A BF**, the NM distinguishes this sample as NMOC, the following 6 characters are additional LIMS numbers, which are followed by a capital letter "A" (replicate code), followed by a single space and then the sample location or other information. The example above is the first replicate of a Bakersfield sample having a LIMS number of NM000125A.

**Turbochrom Method File: CHANNEL A: Calibration Method for DB-1 Analysis**

**Turbochrom Method File: C:\TC4-2F12\DATA22\HC22.MTH**

Created by: SSR on: 6/7/99 04:09 PM  
Edited by: SSR on: 1/31/00 11:53 AM

Description: **NMOC SPECIATED INSTRUMENT D (hc22)**

**Instrument Control Method:**  
Instrument name: **HC22D**

**Interface Parameters:**

Delay Time : 0.00 min.  
Run Time : 60.00 min.  
Sampling Rate : 2.0000 pts/s  
Interface Type : 900  
Analog Voltage Input: 1000 mV  
Data will be collected from both channels

**Timed Events:**

There are no timed events in the method

**Real Time Plot Parameters:**

Channel A Pages: 1 Offset: 0.100 mV Scale: 10.000 mV

**Processing Parameters:**

Bunch Factor : 4 points  
Noise Threshold : 5 uV  
Area Threshold : 24.00 uV

**Peak Separation Criteria**

Width Ratio : 0.200  
Valley-to-Peak Ratio : 0.010

**Exponential Skim Criteria**

Peak Height Ratio : 5.000  
Adjusted Height Ratio : 4.000  
Valley Height Ratio : 3.000

**Baseline Timed Events:**

Event #1 - -P at 0.000  
Event #2 - +P at 9.000

**Annotated Replot Parameters:**

Offset will be autozeroed  
Plot Scale: 15.000 mV  
Start Time : 7.00  
End Time : 50.00

**Component Information:**

**3-MeButene**

Component Type: Single Peak Component  
Retention Time: 9.100 min Search Window: 0.00 s, 3.00 %  
Reference Component: 2-MeButane  
Find largest peak in window  
Quantitation will be done using  $R_f=1.000000$

**2-MeButane**

Component Type: Single Peak Component  
Retention Time: 9.380 min Search Window: 0.00 s, 2.00 %  
Find peak closest to expected RT in window  
Quantitation will be done using  $R_f = 1.000000$

**1-Pentene**

Component Type: Single Peak Component  
Retention Time: 10.01 min Search Window: 0.00 s, 2.00 %

Reference Component: 2-MeButane

Find largest peak in window  
Quantitation will be done using  $R_f = 1.000000$

***Pentane***

Component Type: Single Peak Component  
Retention Time: 10.52 min Search Window: 0.00 s, 2.00 %  
Reference Component: 2-MeButane  
Find largest peak in window  
Quantitation will be done using  $R_f = 1.000000$

***Isoprene***

Component Type: Single Peak Component  
Retention Time: 10.71 min Search Window: 0.00 s, 2.00 %  
Reference Component: 2-MeButane  
Find largest peak in window  
Quantitation will be done using  $R_f = 1.000000$

***t-2-Pentene***

Component Type: Single Peak Component  
Retention Time: 10.89 min Search Window: 0.00 s, 2.00 %  
Reference Component: 2-MeButane  
Find largest peak in window  
Quantitation will be done using  $R_f = 1.000000$

***c-2-Pentene***

Component Type: Single Peak Component  
Retention Time: 11.25 min Search Window: 0.00 s, 2.00 %  
Reference Component: 2-MeButane  
Find largest peak in window  
Quantitation will be done using  $R_f = 1.000000$

***2-Me-2-Butene***

Component Type: Single Peak Component  
Retention Time: 11.48 min Search Window: 0.00 s, 2.00 %  
Reference Component: 2-MeButane  
Find peak closest to expected RT in window  
Quantitation will be done using  $R_f = 1.000000$

***2,2-DiMeButane***

Component Type: Single Peak Component  
Retention Time: 12.24 min Search Window: 0.00 s, 2.00 %  
Reference Component: 2-MeButane  
Find largest peak in window

Quantitation will be done using  $R_f = 1.000000$

**Cyclopentene**

Component Type: Single Peak Component  
Retention Time: 12.64 min Search Window: 0.00 s, 0.50 %  
Reference Component: 2-MeButane  
Find largest peak in window  
Quantitation will be done using  $R_f = 1.000000$

**4MPente/3MPente**

Component Type: Single Peak Component  
Retention Time: 13.16 min Search Window: 0.00 s, 0.50 %  
Reference Component: Benzene  
Find largest peak in window  
Quantitation will be done using  $R_f = 1.000000$

**Cyclopentane**

Component Type: Single Peak Component  
Retention Time: 13.73 min Search Window: 0.00 s, 1.00 %  
Reference Component: Benzene  
Find peak closest to expected RT in window  
Quantitation will be done using  $R_f = 1.000000$

**2,3-DiMeButane**

Component Type: Single Peak Component  
Retention Time: 13.89 min Search Window: 0.00 s, 1.50 %  
Reference Component: Benzene  
Find largest peak in window  
Quantitation will be done using  $R_f = 1.000000$

**2-MePentane**

Component Type: Single Peak Component  
Retention Time: 14.17 min Search Window: 0.00 s, 2.00 %  
Reference Component:  
Find peak closest to expected RT in window  
Quantitation will be done using  $R_f = 1.000000$

**3-MePentane**

Component Type: Single Peak Component  
Retention Time: 14.99 min Search Window: 0.00 s, 2.00 %  
Reference Component: Benzene  
Find largest peak in window  
Quantitation will be done using  $R_f = 1.000000$

**Hexane**

Component Type: Single Peak Component  
Retention Time: 16.05 min Search Window: 0.00 s, 2.00 %  
Reference Component: Benzene  
Find largest peak in window  
Quantitation will be done using  $R_f = 1.000000$

***t*-2-Hexene**

Component Type: Single Peak Component  
Retention Time: 16.35 min Search Window: 0.00 s, 0.50 %  
Reference Component:  
Find peak closest to expected RT in window  
Quantitation will be done using  $R_f = 1.000000$

**2-Me-1-Pentene**

Component Type: Single Peak Component  
Retention Time: 16.48 min Search Window: 0.00 s, 2.00 %  
Reference Component:  
Find largest peak in window  
Quantitation will be done using  $R_f = 1.000000$

***c*-2-Hexene**

Component Type: Single Peak Component  
Retention Time: 16.69 min Search Window: 0.00 s, 0.50 %  
Reference Component: Benzene  
Find largest peak in window  
Quantitation will be done using  $R_f = 1.000000$

**MeCyclopentane**

Component Type: Single Peak Component  
Retention Time: 17.60 min Search Window: 0.00 s, 1.50 %  
Reference Component: Benzene  
Find largest peak in window  
Quantitation will be done using  $R_f = 1.000000$

**2,4-DiMePentane**

Component Type: Single Peak Component  
Retention Time: 17.94 min Search Window: 0.00 s, 2.00 %  
Reference Component:  
Find largest peak in window  
Quantitation will be done using  $R_f = 1.000000$

**2,2,3-TriMeButane**

Component Type: Single Peak Component

Retention Time: 18.29 min Search Window: 0.00 s, 0.50 %

Reference Component: Benzene

Find largest peak in window

Quantitation will be done using  $R_f = 1.000000$

**Benzene**

Component Type: Single Peak Component

Retention Time: 19.08 min Search Window: 0.00 s, 1.50 %

Reference Component:

Find largest peak in window

Quantitation will be done using  $R_f = 1.000000$

**Cyclohexane**

Component Type: Single Peak Component

Retention Time: 19.67 min Search Window: 0.00 s, 1.50 %

Reference Component: Benzene

Find largest peak in window

Quantitation will be done using  $R_f = 1.000000$

**2-MeHexane**

Component Type: Single Peak Component

Retention Time: 20.33 min Search Window: 0.00 s, 0.30 %

Reference Component: Benzene

Find largest peak in window

Quantitation will be done using  $R_f = 1.000000$

**2,3-DiMePentane**

Component Type: Single Peak Component

Retention Time: 20.41 min Search Window: 0.00 s, 0.30 %

Reference Component: Benzene

Find largest peak in window

Quantitation will be done using  $R_f = 1.000000$

**3-MeHexane**

Component Type: Single Peak Component

Retention Time: 20.88 min Search Window: 0.00 s, 1.50 %

Reference Component: Benzene

Find largest peak in window

Quantitation will be done using  $R_f = 1.000000$

**c-1,3-DiMeCycPenta**

Component Type: Single Peak Component



Retention Time: 21.08 min Search Window: 0.00 s, 0.50 %  
Reference Component: Benzene

Find peak closest to expected RT in window  
Quantitation will be done using  $R_f = 1.000000$

***t-1,3-DiMeCycPenta***

Component Type: Single Peak Component  
Retention Time: 21.38 min Search Window: 0.00 s, 0.10 %  
Reference Component: Benzene  
Find peak closest to expected RT in window  
Quantitation will be done using  $R_f = 1.000000$

***2,2,4-TriMePentane***

Component Type: Single Peak Component  
Retention Time: 21.72 min Search Window: 0.00 s, 1.50 %  
Reference Component: Toluene  
Find largest peak in window  
Quantitation will be done using  $R_f = 1.000000$

***Heptane***

Component Type: Single Peak Component  
Retention Time: 22.45 min Search Window: 0.00 s, 1.50 %  
Reference Component: Toluene  
Find largest peak in window  
Quantitation will be done using  $R_f = 1.000000$

***MeCyclohexane***

Component Type: Single Peak Component  
Retention Time: 23.70 min Search Window: 0.00 s, 1.50 %  
Reference Component: Toluene  
Find largest peak in window  
Quantitation will be done using  $R_f = 1.000000$

***2,5-DiMeHexane***

Component Type: Single Peak Component  
Retention Time: 24.74 min Search Window: 0.00 s, 0.50 %  
Reference Component: Toluene  
Find peak closest to expected RT in window  
Quantitation will be done using  $R_f = 1.000000$

***2,3,4-TriMePentane***

Component Type: Single Peak Component  
Retention Time: 25.65 min Search Window: 0.00 s, 1.00 %  
Reference Component: Toluene

Find largest peak in window  
Quantitation will be done using  $R_f = 1.000000$

### ***Toluene***

Component Type: Single Peak Component  
Retention Time: 25.89 min Search Window: 0.00 s, 1.50 %  
Reference Component:  
Find largest peak in window  
Quantitation will be done using  $R_f = 1.000000$

### ***2-MeHeptane***

Component Type: Single Peak Component  
Retention Time: 26.69 min Search Window: 0.00 s, 1.00 %  
Reference Component: Toluene  
Find largest peak in window  
Quantitation will be done using  $R_f = 1.000000$

### ***3-MeHeptane***

Component Type: Single Peak Component  
Retention Time: 27.17 min Search Window: 0.00 s, 1.00 %  
Reference Component: Toluene  
Find largest peak in window  
Quantitation will be done using  $R_f = 1.000000$

### ***3-EtHexane***

Component Type: Single Peak Component  
Retention Time: 27.37 min Search Window: 0.00 s, 0.50 %  
Reference Component: Toluene  
Find peak closest to expected RT in window  
Quantitation will be done using  $R_f = 1.000000$

### ***Octane***

Component Type: Single Peak Component  
Retention Time: 28.81 min Search Window: 0.00 s, 1.50 %  
Reference Component: Toluene  
Find largest peak in window  
Quantitation will be done using  $R_f = 1.000000$

### ***EtBenzene***

Component Type: Single Peak Component  
Retention Time: 31.80 min Search Window: 0.00 s, 1.00 %  
Reference Component: Toluene  
Find peak closest to expected RT in window  
Quantitation will be done using  $R_f = 1.000000$

***m/p-Xylene***

Component Type: Single Peak Component  
Retention Time: 32.39 min Search Window: 0.00 s, 1.00 %  
Reference Component:  
Find largest peak in window  
Quantitation will be done using  $R_f = 1.000000$

***Styrene***

Component Type: Single Peak Component  
Retention Time: 33.44 min Search Window: 0.00 s, 0.50 %  
Reference Component: m/p-Xylene  
Find peak closest to expected RT in window  
Quantitation will be done using  $R_f = 1.000000$

***o-Xylene***

Component Type: Single Peak Component  
Retention Time: 33.75 min Search Window: 0.00 s, 0.50 %  
Reference Component: m/p-Xylene  
Find largest peak in window  
Quantitation will be done using  $R_f = 1.000000$

***Nonane***

Component Type: Single Peak Component  
Retention Time: 34.91 min Search Window: 0.00 s, 1.00 %  
Reference Component: m/p-Xylene  
Find peak closest to expected RT in window  
Quantitation will be done using  $R_f = 1.000000$

***IsopropylBenzene***

Component Type: Single Peak Component  
Retention Time: 35.65 min Search Window: 0.00 s, 1.00 %  
Reference Component: n-PropylBenzene  
Find largest peak in window  
Quantitation will be done using  $R_f = 1.000000$

***n-PropylBenzene***

Component Type: Single Peak Component  
Retention Time: 37.20 min Search Window: 0.00 s, 1.00 %  
Reference Component:  
Find peak closest to expected RT in window  
Quantitation will be done using  $R_f = 1.000000$

***m-EtToluene***

Component Type: Single Peak Component

Retention Time: 37.57 min Search Window: 0.00 s, 0.30 %

Reference Component: 1,2,4-TriMeBenzene

Find peak closest to expected RT in window

Quantitation will be done using  $R_f = 1.000000$

***p-EtToluene***

Component Type: Single Peak Component

Retention Time: 37.68 min Search Window: 0.00 s, 0.30 %

Reference Component: 1,2,4-TriMeBenzene

Find largest peak in window

Quantitation will be done using  $R_f = 1.000000$

***1,3,5-TriMeBenzene***

Component Type: Single Peak Component

Retention Time: 37.95 min Search Window: 0.00 s, 0.50 %

Reference Component: 1,2,4-TriMeBenzene

Find largest peak in window

Quantitation will be done using  $R_f = 1.000000$

***o-EtToluene***

Component Type: Single Peak Component

Retention Time: 38.44 min Search Window: 0.00 s, 1.00 %

Reference Component: 1,2,4-TriMeBenzene

Find largest peak in window

Quantitation will be done using  $R_f = 1.000000$

***1,2,4-TriMeBenzene***

Component Type: Single Peak Component

Retention Time: 39.15 min Search Window: 0.00 s, 0.50 %

Reference Component:

Find largest peak in window

Quantitation will be done using  $R_f = 1.000000$

***Decane***

Component Type: Single Peak Component

Retention Time: 39.87 min Search Window: 0.00 s, 0.50 %

Reference Component: 1,2,4-TriMeBenzene

**Turbochrom Method File: CHANNEL B: Calibration Method for PLOT Analysis**

**Turbochrom Method File: C:\TC4-2F12\DATA22\IC22.MTH**

**Instrument Conditions: NMOC SPECIATED INSTRUMENT D (IC22)**

**Instrument Control Method: Instrument name: HC22D**

**Interface Parameters:**

Delay Time : 0.00 min.  
Run Time : 50.00 min.  
Sampling Rate : 2.0000 pts/s  
Interface Type : 900  
Analog Voltage Input: 1000 mV  
Data will be collected from both channels

**Timed Events:**

There are no timed events in the method

**Real Time Plot Parameters:**

Channel A -- Pages: 3 Offset: 0.100 mV Scale: 10.000 mV  
Channel B -- Pages: 3 Offset: 0.100 mV Scale: 10.000 mV

**Processing Parameters:**

Bunch Factor : 2 points  
Noise Threshold : 9 uV  
Area Threshold : 45.00 uV

**Peak Separation Criteria**

Width Ratio : 0.200  
Valley-to-Peak Ratio : 0.010

**Exponential Skim Criteria**

Peak Height Ratio : 5.000  
Adjusted Height Ratio : 4.000  
Valley Height Ratio : 3.000

**Baseline Timed Events:**

Event #1 - -P at 0.000  
Event #2 - +P at 4.800

**Annotated Replot Parameters:**

Offset will be autozeroed  
Plot Scale: 10.000 mV  
Number of Pages: 1

Plot Title: Chromatogram  
X-Axis Label: Time [min]

y-axes Label: Response [mV]  
Orientation: Landscape  
Retention Labels: Top of Plot  
Component Labels: Actual Time  
Start Time: 3.00  
End Time: 50.00

**Report Format files:**

No report format files given

**User Programs:**

No user programs will be executed

**Global Information:**

Default Sample Volume: 1.000 ppb C  
Quantitation Units: ppb C  
Void Time: 0.000 min  
Correct amounts during calibration: YES  
Reject outliers during calibration: NO  
An External Standard calibration will be used  
Unknown peaks will be quantitated using a Rf of 1.000000

**Component Information:**

***Ethane***

Component Type: Single Peak Component  
Retention Time: 5.67 min Search Window: 0.00 s, 5.00 %  
Reference Component: Propane  
Find largest peak in window  
Quantitation will be done using Rf = 1.000000

***Ethene***

Component Type: Single Peak Component  
Retention Time: 9.20 min Search Window: 0.00 s, 5.00 %  
Reference Component: Propane  
Find peak closest to expected RT in window  
Quantitation will be done using Rf = 1.000000

***Propane***

Component Type: Single Peak Component  
Retention Time: 13.09 min Search Window: 0.00 s, 5.00 %  
Reference Component:

Find largest peak in window  
Quantitation will be done using  $R_f = 1.000000$

***Propene***

Component Type: Single Peak Component  
Retention Time: 22.41 min Search Window: 0.00 s, 1.00 %  
Reference Component: Propane  
Find largest peak in window  
Quantitation will be done using  $R_f = 1.000000$

***Isobutane***

Component Type: Single Peak Component  
Retention Time: 23.98 min Search Window: 0.00 s, 1.00 %  
Reference Component: Propane  
Find largest peak in window  
Quantitation will be done using  $R_f = 1.000000$

***Butane***

Component Type: Single Peak Component  
Retention Time: 25.20 min Search Window: 0.00 s, 1.00 %  
Reference Component: Propane  
Find largest peak in window  
Quantitation will be done using  $R_f = 1.000000$

***Ethyne***

Component Type: Single Peak Component  
Retention Time: 28.82 min Search Window: 0.00 s, 3.00 %  
Reference Component: Propane  
Find largest peak in window  
Quantitation will be done using  $R_f = 1.000000$

***t-2-Butene***

Component Type: Single Peak Component  
Retention Time: 31.85 min Search Window: 0.00 s, 0.50 %  
Reference Component: Propane  
Find largest peak in window  
Quantitation will be done using  $R_f = 1.000000$

***1-Butene***

Component Type: Single Peak Component  
Retention Time: 32.55 min Search Window: 0.00 s, 0.50 %  
Reference Component: Propane  
Find largest peak in window  
Quantitation will be done using  $R_f = 1.000000$

**Isobutene**

Component Type: Single Peak Component  
Retention Time: 33.83 min Search Window: 0.00 s, 1.00 %  
Reference Component: Propane  
Find peak closest to expected RT in window  
Quantitation will be done using Rf = 1.000000

**c-2-Butene**

Component Type: Single Peak Component  
Retention Time: 34.59 min Search Window: 0.00 s, 3.00 %  
Reference Component:  
Find peak closest to expected RT in window  
Quantitation will be done using Rf = 1.000000

**1,3-Butadiene**

Component Type: Single Peak Component  
Retention Time: 38.80 min Search Window: 0.00 s, 3.00 %  
Reference Component: Propane  
Find largest peak in window  
Quantitation will be done using Rf = 1.000000

**SEQUENCE**

---

**Turbochrom Sequence File: C:\tc4-2f12\Data22\Oct05D.SEQ**

Created by: SSR on: 12/21/99 10:15 AM

Edited by: SSR on : 12/21/99 10:15 AM

Description:

**Sequence File Header Information:**

Number of Rows : 5

Instrument Type : 760 / 900 Series Intelligent Interface

Injection Type : NA

**Sequence Sample Descriptions - Channel A**

Row	Sample	Study	ISTD	Method	Raw	Result
1	BLK	Spec_D	1.000	hc22	OC05D001	OC05D001
2	STD33762	Spec_D	1.000	hc22	OC05D002	OC05D002
3	CTL60089	Spec_D	1.000	hc22	OC05D003	OC05D003
4	NM000125	Spec_D	1.000	hc22	OC05D004	OC05D004
5	NM000125A	Spec_D	1.000	hc22	OC05D005	OC05D005



### Sequence Sample Descriptions - Channel B

Row	Sample	Study	ISTD	Method	Raw	Result
1	BLK	Spec_D	1.000	ic22	PC05D001	PC05D001
2	STD33762	Spec_D	1.000	ic22	PC05D002	PC05D002
3	CTL60089	Spec_D	1.000	ic22	PC05D003	PC05D003
4	NM000125	Spec_D	1.000	ic22	PC05D004	PC05D004
5	NM000125A	Spec_D	1.000	ic22	PC05D005	PC05D005

### **APPENDIX III**

#### **VARIAN STAR CHROMATOGRAPHY WORKSTATION**

The Varian Star Chromatography Workstation operates under Windows 95. The Star Chromatography Workstation controls the GC instruments, automates data collection and analysis, and documents the results of a chromatographic run. It uses four primary applications to perform specific tasks:

1. System Control and Automation
2. Method Editor
3. Interactive Graphics and Data Handling
4. Reports

The Interactive Graphics/Data Handling and Report Generating will not be addressed here since PE Nelson 2700 Data System (Turbochrom) is the primary interactive software used at this time. Also, the scope of Appendix III is directed only for speciated NMOC analysis and only addresses set parameters for Method MLD032. For general application of Star Workstation software, please refer to the Ultra Trace Hydrocarbon System Operator's Manual by Lotus Consulting (1993).

#### **System Control and Automation: Part 1**

This is the 1<sup>o</sup> station for the instrument. It reports on the status of the instrument and on its configuration. It also allows you to run methods for a particular set of samples. From this window, one can access and edit three main types of files: method file (\*.mth), sample file (\*.smp), and sequence file (\*.seq).

The basic configuration for GC Star Workstation consists of up to four GC systems, with one Analog-to-Digital Converter (ADC) Board installed in the PC for each GC (i.e., each GC is cabled to its own ADC Board). Before any sample injection can be made, the instrument must be properly configured. The bus address of each module appears at the bottom of its icon. The bus address of GC3600 (Instrument Control/Auto Control Module box) should always be one number greater than the bus address of its ADC Board.

Method MLD032 is configured with instrument #2, which is identified as Varian 3600Cx – NMOC22. Auto Control Module Address GC3600 23 and ADCB Address 22 are set addresses and are also configured with instrument #1. To configure or to confirm the configuration of the instrument, click mouse cursor on 'Instrument' and set the following parameters for instrument #1:

Instrument : HC122D  
Operator : Your Name  
Max Errors : 99 (number of non-fatal errors)

Open Instrument #1/HC22D: 'System Control - Varian 3600 –HC22D - Status' - window that the operator will usually monitor during the run. It provides the current status of the instrument and allows one to access and to modify all the system parameters for a sample run.

Open 'File'Sequence File  
    Method File  
    Sample ListFile  
    Sample Log File  
    Printer Setup...  
    Save Active Method...  
    Exit

Open 'Method File'...  
    New...  
    Open...

Select New or Open depending upon whether method **NMOC22.mth** already exists as a file. By taking the steps listed above, the operator has entered into the Method Editor. Note: Any of the 4 major functions can be accessed from another active function.

### **Method Editor:**

**Edit NMOC22.MTH:**

1. ADCBoard-Module 22
2. ADCBoard-Data Handling-Module 22.A\*
3. ADCBoard-Data Handling-Module 22.B\*
4. 3600GC-Module 23

\* Not used

**1. Open 3600GC-Module 23:**

- 3600 GC Injector
- 3600 GC Auxiliary
- 3600 GC Column
- 3600 GC Detectors
- 3600 AutoSampler
- 3600 GC Relays
- 3600 GC Stripchart

Edit each of the items listed for 3600 Module - 23 and set the parameters listed below:

**3600 GC Injector A:**

Injector Type : Temperature Programmable  
Injector Heater : Off  
Initial Temp. : 50°C  
Hold Time : 0.00 minutes

**3600 GC Injector B:**

Injector Type : Temperature Programmable  
Injector Heater : On  
Initial Temp. : -172°C (set -72)  
Hold Time : 0.50 minutes

Temp. Program 1

Rate : 250°C/min.  
Final Temp. : 200°C (set at 250)  
Hold Time : 58.0 min.  
Coolant valve : On  
Coolant timeout : 60.00 min.

**GC Auxiliary:**

Auxiliary Type : Isothermal  
Auxiliary Heater : On  
Description : Valves B,C,D  
Initial Temp. : 175°C  
Hold Time : 0.00 min.

**3600 GC Column:**

Column Oven : On  
Initial Temp. : 0°C  
Hold Time : 2.00 min.  
Stabilization : 2.00 min.  
Coolant to Column : On  
Coolant Timeout : 60.00 min.

Column Program 1

Rate : 3°C/min.  
Final Temp. : 90°C  
Hold Time: 1.00 min.

Column Program 2

Rate : 5°C/min.

Final Temp. : 200°C  
Hold Time : 5.00 min.

### 3600 GC Detectors:

Detect. Heater : On  
Set Temp. : 250°C  
Detector Type A : FID (On)  
Detector Type B : Not used (Off)  
Time Program : No  
Detector Type A : Range 12  
Attenuation : 8\*  
A/Z On : Yes

**\*Note:** The attenuation value in the 3600 GC detectors window changes the output signal to the stripchart recorder. We are currently not using the stripchart recorder and therefore the attenuation setting is not applicable in our method.

### 3600 AutoSampler:

AutoSampler Type: 8134 SSV

Note: Up to 16 samples can be analyzed with the optional multi-position automated sampler. Separate external temperature control is used to heat the autosampler 130°C.

### 3600 GC Relays: Relay Time Program: Use

<u>Time</u>	<u>Relays</u>
0.00 min.	- - - -
0.01 min.	- - - <b>+4</b>
1.50 min.	- - - -
3.40 min.	<b>+1</b> - - -

[X] Return Relays to Initial Cond. at End Run

**3600 GC Stripchart:** Stripchart :Off  
Time Program :No

## 2. Open ADCBoard - Module 22

ADCB - Set Conditions (set end time for run)  
ADCB Detector Information (doc. of detectors)

**ADCB - Set Cond.**

End Time : 60.00 minutes  
Channel A : FID  
Channel B : FID  
Channel A Full Scale : Alumina  
Channel B Full Scale : DB-1  
Zero Display at the Start : Yes

**Detector Info.**

Detector Bunch Rate : 8 pts (5Hz)  
Noise Monitor Length : 64 bunched points  
Data File Name : MMDDDD \*

\* MM = Month; DD = Day; **D** =designated for MLD032 HC22  
I.e., MR01B = March 01 MLD032 NMOC speciated analysis

**Edit Bakeout22.MTH**

1. 3600GC-Module 23

2. ADCBoard-Data Handling-Module 22.A\*

3. ADCBoard-Data Handling-Module 22.B\*

\* Not used

**Note:** *For convenience and the ease of creating a new method, copy NMOC22.MTH and edit only the following parameters listed below. Save method as **Bakeout22.mth**.*

**3600 GC Injector A:** Injector Type: : Temperature Programmable  
Oven on : no  
Initial Temp. : 50°C  
Hold Time : 0.00 minutes  
Coolant Time Out. : Infinite  
End Time : 69.00 min.

**3600 GC Injector B:** Injector Type: : Temperature Programmable  
Initial Temp. : 250°C  
Hold Time : 69.00 minutes  
Oven on : yes  
Coolant Time Out. : Infinite

**3600 GC Auxiliary:** Injector Type : Isothermal  
Oven on : Yes  
Initial Temp. : 175°C  
Hold Time : 0.00 minutes

**3600 GC Column:** Column Oven : On  
Initial Temperature : 50°C  
Hold Time : 0.00 minutes  
Thermal Stabilization: 2.00 minutes  
GC Coolant Column : No  
Coolant Time Out : Infinite

Column Program 1

Rate : 30°C/min.  
Final Temp. : 200°C  
Hold Time : 64.00 min.

**3600 GC Detectors:** Same as NMOC22.mth.

**3600 GC AutoSampler:** Same as NMOC22.mth.

**3600 GC Relays:** Relay Time Program: Use  

<u>Time</u>	<u>Relays</u>			
0.00 min.	+1	-2	-3	-4

  
[X] Return Relays to Initial Cond. at End Run

**3600 GC Stripchart:** Same as NMOC22.mth.

**Detector Info** Data File Name : Star

**Edit Idle22.MTH**

1. 3600GC-Module 23
  2. ADCBoard-Data Handling-Module 22.A\*
  3. ADCBoard-Data Handling-Module 22.B\*
- \* Not used

Note: For convenience and the ease of creating a new method, copy NMOC22.MTH and edit only the following parameters listed below. Save method as **Idle22.mth**.

**3600 GC Injector A:** Injector Type : Temperature Programmable

Oven on : No

Initial Temp. : 50°C  
Hold Time : 0.00 minutes  
Coolant Time Out. : Infinite  
End Time : 69.00 min.

**3600 GC Injector B:** Injector Type: : Temperature Programmable  
Initial Temp. : 250°C  
Hold Time : Infinite  
Oven on : Yes  
Coolant Time Out. : 30.00 minutes

**3600 GC Auxiliary:** Same as NMOC16.mth

**3600 GC Column:** Initial Temp. : 100°C  
Hold Time : Infinite  
Therm. Stabilization: 2.00 minutes  
Coolant to Column : Yes  
Coolant Time Out : 30.00 minutes

**3600 GC Detectors:** Same as NMOC22.mth

**3600 AutoSampler:** Same as NMOC22.mth

**3600 GC Relays:** Relay Time Program : Use +1

**3600 GC Stripchart:** Same as NMOC22.mth

**Detector Info:** Data File Name : Idle

## **System Control and Automation: Part 2**

In the 'System Control - Varian 3600 – HC22D window it is time to build a SampleList file and a Sequence file.

**Edit SampleList File:** New...Sample List Selection Type: 8134 SSV

### **NMOC22D.SMP:**

Sample list or Sample File list is required by System Control for identifying what kind of sample is being injected and the order of



sample injection (when performing a series of injections). In the

displayed 'NMOC22D.SMP-SampleList' window there are the following parameters that need to be defined:

1. Sample Name
2. Sample Type
3. Cal. Level
4. # Inj.
5. Injection Notes
6. AutoLink
7. Stream
8. Relay Program
9. Amount Std.
10. Unidentified Peak Factor
11. Multiplier
12. Divisor

1. Sample Name: Use same format for base names as in PE Nelson 2700 Data System (Appendix I).

2. Sample Type: Use 'Analysis' as default for all samples. The system calibration and report generation will be done by PE Nelson 2700 Data System (Appendix I).

3. Cal. Level: Not applicable - all samples are set for analysis. Calibration is done by PE Nelson 2700 Data System (Appendix I).

4. # Inj.: Allows you to set the number of injections (i.e., number of analysis) to be performed on that particular sample.

5. Injection Notes: User defined

6. AutoLink: NA

7. Stream: Identify the port (stream) number for the corresponding sample.

8. Relay Program: Discussed below in text.

9. Amount Std: Use 1.0000 as a default value.

10. Unidentified Peak Factor: Use 0.0000 as a default value.

11. Multiplier: Use 1.0000 as a default value.

12. Divisor: Use 1.0000 as a default value.

**Note:** *These values are set in the 'Defaults...' window (click on the default button in the SampleList window). These parameters are common to all entries in the Sample List with the exceptions of Sample Name, # Inj., and Stream, which are edited directly in the SampleList window.*

8. Relay Program: In the 'Defaults...' window click on 'Relays...' button and open '8134 SSV Relay Program'. A 300 sccm aliquot of standard, control or ambient air sample is introduced into the GC

from the automated preconcentration system by means of the relay time program set below as follows:

<u>Time (min.)</u>	<u>Relay</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
0.00	-	-	-	-	-
0.01	-	-	<b>+3</b>	-	-
1.00	-	<b>+2</b>	<b>+3</b>	-	-
7.00	-	<b>+2</b>	-	-	-
7.30	-	<b>+2</b>	-	<b>+4</b>	-
7.35	-	-	-	-	<b>+4</b>

Note:(-) sign = off position; (+) sign = on position

Save or update the default settings, and return to the 'NMOC16B.SMP - SampleList' window. Complete the sample list and Save as...NMOC22D.SMP.

Note: To run a dilution of a particular sample or a multipoint analysis of speciated NMOC analytes, edit the relay time program in the NMOC22D.SMP. as follows:

1. Identify the sample that requires dilution.
2. Identify the stream that the particular sample is attached to.
3. Log-in the sample in the SampleList, using default parameters.
4. Click on the stream number (select with mouse) and edit the relays in the SampleList window. Do not edit the relays under the default window because these are set for 300 cc sample volume common to all entries in the SampleList.
5. Edit the time between activating Valve B (**+3**) and turning off Valve B (**-3**), thus varying the effective sample loading. Leave

other time events as default values.

6. Save the changes made. Only the selected stream will have saved edited parameters, whereas the rest of the samples in the SampleList file will have default values.

### **Bakeout22.SMP:**

Bakeout16.smp is a sample file that is appended to Bakeout22.MTH. Bakeout16.mth calls for injection of the sample and requires a separate sample file that has defined parameters that differ from the .SMP file discussed above. In the New...SampleList window, log in the name of the sample as 'Bakeout' sample. Use all the default values (as discussed previously) and edit Relays...:

<u>Time (min.)</u>	<u>Relay</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
0.00		+1	-	-	-

All the relays are in off-position except for valve A (+1), and no sample is injected into the column (sample flow dead-ends, N<sub>2</sub>-purge gas flows through the mass flow controller and flow meter and He-carrier gas flows through the cold trap and through the column to the detector). Valve A is on to keep the trap in series with the DB-1 column, as to prevent any external contamination of the PLOT column. The purpose of the "Baking-out" the system is to remove any contamination (e.g., volatile and semi-volatile residues) by elevating the temperatures of different temperature zones for short periods of time.

### **Idle22.SMP:**

Create an Idle sample list file for Idle22.mth by copying the Bakeout16.smp and Save As Idle22.smp.

### **Edit New Sequence:**

The Sequence (\*.seq) file is responsible for the coordination and execution of a number of operations. The \*.seq file consists of list of \*.mth file/\*.smp file pairs in order of execution. By applying different strategies in building the \*.seq file, one can:

1. Run each SampleList using a different method
2. Run a series of Sample Lists using the same method
3. Run one Sample List run by variety of methods

In the new Sequence window, click on desired cell in the column. The default path is displayed with a file name that is highlighted. Either type

in the path name or use a Browse button. The typical .SEQ for NMOC22D.SEQ run is as follows:

<b>Method</b>	<b>SampleList/Log</b>	<b>Action</b>
1. C:\Star\NMOC22.MTH	C:\Star\NMOC22D.SMP	Inject
2. C:\Star\Idle22.MTH	C:\Star\Idle22D.SMP	Inject

Select the File and Save As...NMOC22D.SEQ. To activate a .SEQ, select File/Sequence File (NMOC22D.SEQ) and Activate a System Control Sequence dialog box. When a sequence is started, System Control performs a series of checks on the method and SampleList files. If any of these checks fails, System Control aborts the \*.seq and indicates the cause within message boxes or entries to the Sequence Log.